PA 1540868

# THE UNITED STATES OF AMERICA

## TO ALL TO WHOM THESE PRESENTS SHALL COME;

**UNITED STATES DEPARTMENT OF COMMERCE**

**United States Patent and Trademark Office**

**November 14, 2006**

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APPLICATION NUMBER: *60/537,115*
FILING DATE: *January 16, 2004*

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS *US60/537,115*

By Authority of the
Under Secretary of Commerce for Intellectual Property
and Director of the United States Patent and Trademark Office

M. K. CARTER
Certifying Officer

# PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

| Express Mail Label No. | EU417945354US |
|---|---|

U.S. PTO
31353
60/537115
011604

## INVENTOR(S)

| Given Name (first and middle [if any]) | Family Name or Surname | Residence (City and either State or Foreign Country) |
|---|---|---|
| Bruce F. <br> James K. | Monzyk <br> Rose | Delaware, Ohio <br> Millersport, Ohio |

Additional inventors are being named on the _____1_____ separately numbered sheets attached hereto

## TITLE OF THE INVENTION (500 characters max)

Apparatus For Producing Ferrate (VI) and Method For Producing Same

### CORRESPONDENCE ADDRESS

Direct all correspondence to:

[✔] Customer Number: 24116

OR

| [ ] Firm or Individual Name | |
|---|---|
| Address | |
| Address | |

| City | | State | | Zip | |
|---|---|---|---|---|---|
| Country | | Telephone | | Fax | |

## ENCLOSED APPLICATION PARTS (check all that apply)

[✔] Specification *Number of Pages* __37__

[✔] Drawing(s) *Number of Sheets* __35__

[✔] Application Data Sheet. See 37 CFR 1.76

[ ] CD(s), Number _____

[ ] Other (specify) _____

## METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

[ ] Applicant claims small entity status. See 37 CFR 1.27.

[ ] A check or money order is enclosed to cover the filing fees.

[ ] The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: _____

[✔] Payment by credit card. Form PTO-2038 is attached.

FILING FEE
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160.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

[✔] No.

[ ] Yes, the name of the U.S. Government agency and the Government contract number are: _____

[Page 1 of 2]

Respectfully submitted _____(signature)_____

SIGNATURE _____(signature)_____

TYPED or PRINTED NAME Klaus H. Wiesmann

TELEPHONE 614-424-6589

Date 1/16/2004

REGISTRATION NO. 30,437
*(if appropriate)*
Docket Number: 22114(1)P

## PROVISIONAL APPLICATION COVER SHEET
### Additional Page

| Docket Number | 22114(1)P |
|---|---|

| INVENTOR(S)/APPLICANT(S) | | |
|---|---|---|
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| Timothy O. | Clark | Lancaster, Ohio |
| Andrew | Smeltz | Athens, Ohio |
| Dennis G. | Rider | Pataskala, Ohio |

[Page 2 of 2]

Number _____1_____ of_____1_____

PTO/SB/17 (10-03)
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# FEE TRANSMITTAL
## for FY 2004

*Effective 10/01/2003. Patent fees are subject to annual revision.*

☐ Applicant claims small entity status. See 37 CFR 1.27

| **TOTAL AMOUNT OF PAYMENT** | ($) 160.00 |

**Complete if Known**

| Application Number | Unknown |
|---|---|
| Filing Date | 01/16/2004 |
| First Named Inventor | Monzyk et al. |
| Examiner Name | |
| Art Unit | |
| Attorney Docket No. | 22114(1)P |

## METHOD OF PAYMENT *(check all that apply)*

☐ Check  ☑ Credit card  ☐ Money Order  ☐ Other  ☐ None

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Deposit Account Name: _____

The Director is authorized to: *(check all that apply)*

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☐ Charge any additional fee(s) or any underpayment of fee(s)

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## FEE CALCULATION

### 1. BASIC FILING FEE

| Large Entity Fee Code | Fee ($) | Small Entity Fee Code | Fee ($) | Fee Description | Fee Paid |
|---|---|---|---|---|---|
| 1001 | 770 | 2001 | 385 | Utility filing fee | |
| 1002 | 340 | 2002 | 170 | Design filing fee | |
| 1003 | 530 | 2003 | 265 | Plant filing fee | |
| 1004 | 770 | 2004 | 385 | Reissue filing fee | |
| 1005 | 160 | 2005 | 80 | Provisional filing fee | 160.00 |

**SUBTOTAL (1)** ($) 160.00

### 2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

| | Extra Claims | | Fee from below | Fee Paid |
|---|---|---|---|---|
| Total Claims | ____ -20** = ____ | x ____ | = ____ | |
| Independent Claims | ____ - 3** = ____ | x ____ | = ____ | |
| Multiple Dependent | | | = ____ | |

| Large Entity Fee Code | Fee ($) | Small Entity Fee Code | Fee ($) | Fee Description |
|---|---|---|---|---|
| 1202 | 18 | 2202 | 9 | Claims in excess of 20 |
| 1201 | 86 | 2201 | 43 | Independent claims in excess of 3 |
| 1203 | 290 | 2203 | 145 | Multiple dependent claim, if not paid |
| 1204 | 86 | 2204 | 43 | ** Reissue independent claims over original patent |
| 1205 | 18 | 2205 | 9 | ** Reissue claims in excess of 20 and over original patent |

**SUBTOTAL (2)** ($) 00

**or number previously paid, if greater; For Reissues, see above

## FEE CALCULATION (continued)

### 3. ADDITIONAL FEES

| Large Entity Fee Code | Fee ($) | Small Entity Fee Code | Fee ($) | Fee Description | Fee Paid |
|---|---|---|---|---|---|
| 1051 | 130 | 2051 | 65 | Surcharge - late filing fee or oath | |
| 1052 | 50 | 2052 | 25 | Surcharge - late provisional filing fee or cover sheet | |
| 1053 | 130 | 1053 | 130 | Non-English specification | |
| 1812 | 2,520 | 1812 | 2,520 | For filing a request for *ex parte* reexamination | |
| 1804 | 920* | 1804 | 920* | Requesting publication of SIR prior to Examiner action | |
| 1805 | 1,840* | 1805 | 1,840* | Requesting publication of SIR after Examiner action | |
| 1251 | 110 | 2251 | 55 | Extension for reply within first month | |
| 1252 | 420 | 2252 | 210 | Extension for reply within second month | |
| 1253 | 950 | 2253 | 475 | Extension for reply within third month | |
| 1254 | 1,480 | 2254 | 740 | Extension for reply within fourth month | |
| 1255 | 2,010 | 2255 | 1,005 | Extension for reply within fifth month | |
| 1401 | 330 | 2401 | 165 | Notice of Appeal | |
| 1402 | 330 | 2402 | 165 | Filing a brief in support of an appeal | |
| 1403 | 290 | 2403 | 145 | Request for oral hearing | |
| 1451 | 1,510 | 1451 | 1,510 | Petition to institute a public use proceeding | |
| 1452 | 110 | 2452 | 55 | Petition to revive - unavoidable | |
| 1453 | 1,330 | 2453 | 665 | Petition to revive - unintentional | |
| 1501 | 1,330 | 2501 | 665 | Utility issue fee (or reissue) | |
| 1502 | 480 | 2502 | 240 | Design issue fee | |
| 1503 | 640 | 2503 | 320 | Plant issue fee | |
| 1460 | 130 | 1460 | 130 | Petitions to the Commissioner | |
| 1807 | 50 | 1807 | 50 | Processing fee under 37 CFR 1.17(q) | |
| 1806 | 180 | 1806 | 180 | Submission of Information Disclosure Stmt | |
| 8021 | 40 | 8021 | 40 | Recording each patent assignment per property (times number of properties) | |
| 1809 | 770 | 2809 | 385 | Filing a submission after final rejection (37 CFR 1.129(a)) | |
| 1810 | 770 | 2810 | 385 | For each additional invention to be examined (37 CFR 1.129(b)) | |
| 1801 | 770 | 2801 | 385 | Request for Continued Examination (RCE) | |
| 1802 | 900 | 1802 | 900 | Request for expedited examination of a design application | |

Other fee (specify) _____

*Reduced by Basic Filing Fee Paid

**SUBTOTAL (3)** ($) 00

## SUBMITTED BY

*(Complete if applicable)*

| Name (Print/Type) | Klaus H. Wiesmann | Registration No. (Attorney/Agent) | 30,437 | Telephone | 614-424-6589 |
|---|---|---|---|---|---|
| Signature | *Klaus H. Wiesmann* | | | Date | 1/16/2004 |

**WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

This collection of information is required by 37 CFR 1.17 and 1.27. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

*If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.*

Practiti ner's Dock t N . _____          **PATENT**

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:  Monzyk et al.
Application No.: 0   /          Group No.:
Filed:     1/16/2004          Examiner:
For:     Apparatus For Producing Ferrate (VI) and Method For Producing Same

Commissioner for Patents
P.O. Box 1450
Alexandria., VA 22313-1450

### EXPRESS MAIL CERTIFICATE

"Express Mail" label number ____EU417945354US____

Date of Deposit ____01/16/2004____

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Provisionla Application Cover Sheet
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Fee Transmittal (in duplicate)
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— KLAUS H. WIESMANN
_____
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*Klaus H. Wiesmann*
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(Express Mail Certificate [8-3])

# PROVISIONAL PATENT APPLICATION

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              Rose, James K.        Millersport, OH
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TITLE:        APPARATUS FOR PRODUCING FERRATE (VI) AND
              METHOD FOR PRODUCING SAME

ATTORNEY:     Klaus H. Wiesmann

REG. NO.:     30,437

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The invention was not made by an agency of the United States Government nor under contract with an agency of the United States Government.

Express Mail No.  EU 417945354  US

APPARATUS FOR PRODUCING FERRATE (VI) AND METHOD FOR PRODUCING SAME

FIELD OF THE INVENTION

The present invention provides for apparatus and methods for the production of oxymetal ions. A typical end product is stable ferrate(VI). The stable ferrate (VI) product is particularly useful for water decontamination and purification such as in sewage treatment plants and in production of potable water supplies.

BACKGROUND OF THE INVENTION

Previous work demonstrated that the electrochemical route to ferrate (VI)-based materials was very promising in that it required readily available, low cost materials, generated very little waste, seemed amenable to continuous, low cost, production, operated without major process problems of the conventional lab procedure, and appeared to provide a readily scaled production process. However, key difficulties included how to:

(1) avoid premature ferrate product decomposition and by-products;

(2) harvest viable ferrate product without the use of solvents or pluggage of filters; (3) avoid passivation of the anode; (4) avoid problems from impurities in the iron source; and (5) achieve good current efficiencies.

BRIEF DESCRIPTION OF THE INVENTION

Broadly the invention provides for apparatus for producing oxymetal ions (e.g. ferrate) using an electrochemical cell. The electrochemical cell typically includes a container; a cathode chamber within said container; an anode chamber within said container and adjacent to the cathode; a separator that separates the anode chamber from the cathode chamber; and a power supply for generating pulsating direct current and voltage for

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application to said cathode and said anode. Typically, the power supply provides a variable direct current voltage across the anode and cathode. The direct current voltage is typically applied so as to have a peak voltage, Vmax, and a minimum voltage, Vmin. Vmin is typically at least above 0 volts and

5   preferably that required to substantially overcome passivation at the anode.

One aspect of the invention provides a method for producing oxymetal ions (e.g ferrate ions) including the steps of providing an electrolytic cell having an anode and a cathode, wherein the anode contains iron; flowing an alkaline solution selected from the group consisting of NaOH, KOH, and a

10  mixture thereof, through the electrolytic cell and between the electrodes; applying a variable D.C. voltage across the anode and cathode, wherein the variable D.C. voltage varies between a peak voltage, Vmax, above for generating oxymetal ions and a minimum voltage, Vmin, wherein Vmin is at least ) volts and preferably is the voltage required to substantially overcome

15  passivation of the anode. Most preferably the voltage is reduced from Vmax so that current flow is less than 10% of the current at Vmax and most preferably 1% of the current at Vmax. Typically the maximum length of time that the voltage is at Vmax is about 1 minute and the minimum time is about 0.001 seconds. A preferable wave has a frequency of about 0.1 Hz to about

20  480 Hz. A more preferable wave has a frequency of about 1 Hz to about 240 Hz.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of one embodiment of an overall

25  apparatus for production of ferrates.

Figure 2 is a schematic diagram of a laboratory apparatus typical of the invention and used to generate some of the data herein.

Figure 3 is a graph depicting Current Yield (CE) in percent, left vertical scale; potassium ferrate(VI) concentration in mM(FeO4), right vertical scale;

30  the ratio of Fe(total)/Fe(VI) shown as Fe:Fe(VI), left vertical scale; and time in minutes, Time(min), on the horizontal scale.

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Figure 4 is a graph depicting Current Yield (CE) in percent, left vertical scale; potassium ferrate(VI) concentration in mM(FeO4), left vertical scale; the production rate in grams/day of Ferrate(VI), left vertical scale; and time in minutes, Time(min), on the horizontal scale.

5    Figure 5 is a schematic of a typical variable DC voltage according to the invention from an trace recording.

Figure 5A is a schematic illustrating the various aspects of the variable DC voltage according to the invention.

Figure 6 is a graph depicting Current Yield (CE) in percent, left vertical

10    scale; the ratio of Fe(total)/Fe(VI) shown as Fe:Fe(VI), right vertical scale; and time in minutes, Time(min), on the horizontal scale. The decrease in electrolyte volume resulted in an increase in current efficiency (actual, interval) from 1.1 to 3.1%.

Figure 7 is a graph depicting Ferrate (VI) concentration in mM, left

15    hand vertical scale; the Production Rate in g/day, right vertical scale; and Time in minutes, on the horizontal scale.

Figure 8 is a graph depicting Ferrate (VI) concentration in mM, left hand vertical scale; the Production Rate in g/day, right vertical scale; and Time in minutes, on the horizontal scale.

20    Figure 9 is a graph depicting the potassium ferrate production rate, g/day, on the left vertical scale; Current Efficiency in %, on the right vertical scale; the ratio of Fe(total)/Fe(VI) shown as Fe:Fe(VI), right vertical scale; and time in minutes, Time(min), on the horizontal scale.

Figure 10 is a graph depicting Ferrate (VI) concentration in mM, left

25    hand vertical scale; the Production Rate in g/day, right vertical scale; and Time in minutes, on the horizontal scale.

Figure 11 is a scopemeter display of the waveforms used for samples in validation tests. The time at the high voltage (and high current) was about 320 ms or about 32%.

30    Figure 12 is a graph depicting the amount of potassium ferrate (VI) produced in grams, g, left vertical scale; and Time in minutes, on the

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horizontal scale. The linear curve fit was used to determine the production rate.

Figure 13 is a graph depicting Current Yield (CE) in percent, left vertical scale; and time in minutes, Time(min), on the horizontal scale. Current efficiencies are depicted on an interval basis (squares); and on a running average (triangles). The left hand scale also is used for showing the number of moles of electrons/6; data points are shown as diamonds. Six electron transfer is required for the process.

Figure 14 is a graph depicting the ferrate concentration, mM, in electrolyte on the left vertical scale; the ratio of Fe(total)/Fe(VI) shown as Total Fe:Fe(VI) Ratio, right vertical scale; and time in minutes, Time(min), on the horizontal scale. Concentration values were determined from both the 785 and 505 UV peak.

Figure 15 is a schematic drawing of one typical embodiment of the invention having three cathodes and two anodes.

Figure 16 is a graph depicting the production of ferrate where the ferrate (VI) concentration is on the left vertical scale in mM; the current efficiency is on the right vertical scale in %; and the time in minutes is on the horizontal scale. Open squares represent measurements at the 785 nm peak and pone triangles represent measurements at the 505 nm peak. Diamonds. represent current efficiency interval measurements and "x" represents the current efficiency running average.

Figure 17 is a graph showing the results from the production of ferrate(VI). The weight of the potassium ferrate produced is shown on the left vertical scale in grams; the time interval in minutes is shown on the horizontal scale. Ferrate (VI) was harvested at four intervals shown on the graph starting at about ) minutes, 1100 minutes, 2300 minutes and 3900 minutes. The graph shows that harvesting greatly increased the rate of production of potassium ferrate. That is each time the product was removed by filtration or centrifugation, the production rate (increased slope of line) increased over that of the average slope that is depicted by the long straight line.

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Figure 18 is a graph for ferrate(VI) production with current efficiency on the left vertical scale, and time on the horizontal scale.

Figure 19 is a pie plate graph showing the centrifuged salt composition as chemical species averages. A table is included as well as a discussion.

Figure 20 is a schematic diagram of one version of a controller for controlling a power supply for providing appropriate varying DC to the apparatus of the invention.

Figure 21 is a schematic diagram of one version of a controller (that uses a microprocessor) for controlling a power supply for providing appropriate varying DC to the apparatus of the invention.

Figure 22 is a side cutaway view of the electrolytic cell according to the invention showing a typical hanging anode/cathode.

Figure 23 is a cutaway side of the apparatus showing a typical screen spacer.

Figure 24 is a top view of a typical layout for anode/spacer/cathode combinations.

Figure 25 is a side view of a typical anode/cathode/screen showing their relative sizes according to one aspect of the invention.

Figure 26 is a perspective view of electrolyte overflows for an anode and a cathode.

Figure 27is a side view of an "L" shaped flow deflector spacers

Figure 28 is a tip view of the bottom of the tank showing electrolyte feed to the tank.

Figure 29 is a view of the electrode bank showing how dead space can be eliminated at the ends of the tank.

Figure 30 is a view of the tank showing a typical side view of the electrode stack for one embodiment.

Figure 31 is schematic showing electrode side spacers.

Figure 32 is a perspective view of the electrolytic cell according to one aspect of the invention.

Figure 33 is a side view of a typical anode, cathode, screen layout according to another aspect of the invention.

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Figure 34 is a side view of a typical anode, cathode, screen layout according to yet another aspect of the invention.

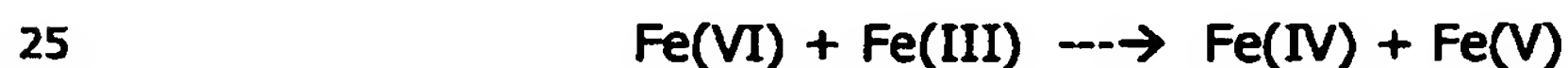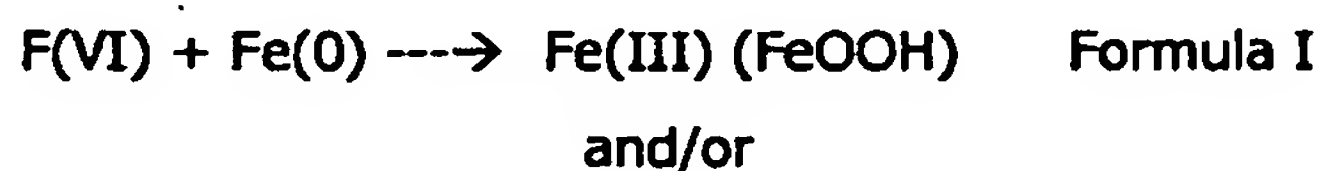Figure 35 is a side view of a typical anode, cathode, screen layout according to another embodiment of the invention.

5    Figure 36 is a side view of the tanks showing the configuration of the catholyte and anolyte overflow ports.

Figure 37 is a side view of a typical anode, cathode, screen layout according to another embodiment of the invention.

Figure 38 is a graph of ferrate(VI) spectra.  Absorption is on the left

10   hand vertical scale and wavelength in nm on the horizontal scale.

Figure 3 is a graph of total iron spectra.  Absorption is on the left hand vertical scale and wavelength in nm on the horizontal scale.

DETAILED DESCRIPTION OF THE INVENTION AND BEST MODE

15   Variable D.C. voltage – as used herein D.C. stands for direct current and has the meaning usually associated therewith in the art.  The voltage will typically not swing substantially below Vmin so as to suppress the formation of  Fe(III) from iron or divalent Fe.

Vmin – as used herein, the voltage across the anode and cathode above

20   which the conversion of Fe(I) or Fe(II) to Fe (III) is substantially depressed. More directly, Vmin is the cell voltage needed to overcome the reaction of

$$F(VI) + Fe(0) \longrightarrow Fe(III) (FeOOH) \qquad \text{Formula I}$$
$$\text{and/or}$$
25
$$Fe(VI) + Fe(III) \longrightarrow Fe(IV) + Fe(V)$$

Vmax – as used herein, the voltage across the anode and cathode that is above the voltage where conversion of lower oxidation states of iron to Fe(VI) is facilitated.  Vmax is typically manifested by the flattening of a variable wave

30   that is superimposed upon a DC voltage.

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Materials useful for the anode comprise iron, manganese, chromium, grey cast iron and the like.

Proposed Chemical Mechanism for Ferrate(VI) Electrochemical Production at the Battelle-Process Conditions

5

PART A: Startup

Generate $O_2$ a few seconds (< 60 seconds) to "blow off" any passivating film from the anode.

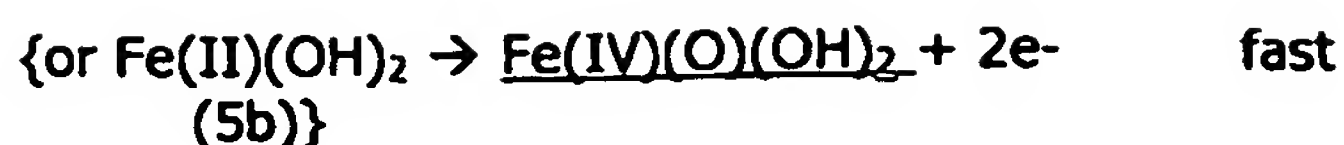10    PART B: Continuous Operation

Two sets of reactions are important; the first one (Electrochemical Oxidation and Dissolution) corresponds to the period when the voltage and current density are high (Vmax, Imax), and the second one (Disproportionation and Dissolution) to when the voltage and current density

15    is at the minimum (Vmin, Imin).

Part B.1: Electrochemical Oxidation and Dissolution of Fe metal
(E.g. at DC "high" conditions: 2.2 volts, 53 Amps, 4-60 mA/cm2):

| Reaction | Estimated Relative Rate | Rx. # |
|---|---|---|
| $Fe(0) + 2OH^- \rightarrow \underline{Fe(II)(OH)_2}^0$ film $+ 2e^-$ | very fast | (1) |
| | (rate determined by applied current density) | |
| $Fe(II)(OH)_2^0 + 2\ OH^- \rightarrow Fe(II)(OH)_4^{2-}$ | very fast | (2) |
| $Fe(II)(OH)_4^{2-} \rightarrow \underline{Fe(III)(OH)_3} + e^-$ | fast | (3) |
| $\underline{Fe(III)(OH)_3} \rightarrow \underline{Fe(IV)(O)(OH)_2} + e^-$ | slow | (4) |
| $Fe(II)(OH)_4^{2-} \rightarrow \underline{Fe(IV)(O)(OH)_2} + 2e^-$ (5a) | fast | |

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{or Fe(II)(OH)$_2$ → Fe(IV)(O)(OH)$_2$ + 2e-       fast
    (5b)}

Fe(IV)(O)(OH)$_2$ → Fe(V)O4$^-$ + e$^-$       slow (RDS)       (6)

Fe(V)O4$^-$ → Fe(V)IO42$^-$ + e$^-$       fast       (7)


Followed by,

Part B.2: Disproportionation and Dissolution

(e.g. at DC "low" conditions: 1.7 volts, 0.4 A, very low current density but not zero):

| Reaction | Estimated Relative Rate | Rx. # |
|---|---|---|
| 2 Fe(IV) → Fe(III) + Fe(V) | medium | (8) |
| 2 Fe(V) → Fe(IV) + Fe(VI) | medium | (9) |

Where the chemical species are of the same representative formulas given in reactions (3) through (7).


The above-proposed chemical mechanism is consistent with both the operating cell data and observations (both batch and continuous, BCO and West Jeff), and the cyclic voltammetry observation (Bouzek literature and Chad's' tests from Jan. 2003). Note that reaction (5) is preferred over the combination of reactions (3) and (4) if reaction (4) is slow (highly probable). That Reaction (5) may be the main path is supported by repeated observations that exceeding a threshold minimum current density appears to produce ferrate at a fast rate, and below this rate ferrate production appears not to proceed rapidly if at all. Batch test results were used to establish the continuous production conditions, which have proven to be very robust (not prone to passivation). Note that reaction (8), and the combined reactions (8) plus (9) correspond to thinning of the iron oxide surface film as the Fe(V) and Fe(VI) products are water-soluble. This film forms from the Fe(II, III, & IV) oxyhydroxides which form in Reactions (1), (3), (4) and (5). Without

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reactions (6) through (9) a thick, non-electrically conducting film would form on the surface of the iron, formed by the oxides produced in reactions 4 and 5, thereby passivating it.

The role of the caustic is clearly seen in this mechanism (balancing the
5    reactions will make it clearer) since the formation of oxides requires OH- ion, and the prevention of protonated species (e.g. $HFeO_4$-) stabilizes the product and favors oxides over hydroxide compounds to form. Perhaps a critical role for the caustic is that it raises the solubility (and hence the mobility and reactivity) of Fe ions normally highly insoluble through anionic complex
10   formation reactions, i.e.

$$\underline{Fe(III)(OH)_3} + OH- \quad \text{-->} \quad Fe(III)O(OH)2- \quad\quad\quad (10)$$
insoluble film                           soluble ion

15   and
$$\underline{Fe(IV)(O)(OH)2} + OH- \quad \text{-->} \quad\quad Fe(IV)O(OH)3- \quad\quad\quad (11)$$
insoluble film                                         soluble ion

Note that the presence of the soluble Fe(V) species rationalizes why
20   the anolyte volume to anode surface area is an important parameter as this ratio determines the time that this reactive species is allowed to exist outside the cell until it is re-introduced to the cell so that it can be oxidized to Fe(VI) by reaction (7). Hence we suggest including a second cell in the anolyte exit to finish the oxidation (Reaction 7) using a non-sacrificial anode such as Pt on
25   Ti or carbon, or a dimensionally stabilized anode (DSA), etc. Lastly, note that, depending on temperature/time/concentration profiles, the Fe(III) species may be best represented as Fe(III)(OH)3 or as Fe(III)OOH. These are taken as chemically equivalent in the above mechanism discussion.

The above mechanism represents a good starting point for any
30   fundamental studies, e.g. using CV, which would be done to enhance the ferrate production rate, product purity, and current efficiency economics further. The literature should also be consulted again to see if the mechanism could be refined further based on the data and previous mechanisms involving ferrate(VI) reported therein. The visible observation

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that ferrate(VI) formation only occurs during a very narrow voltage range and the experimental tests from summer 2002 which indicates that Vmin should never be zero or below (i.e. AC is not desirable), and the very productive data received for the Vmin~ 1.7 volts (Dec '02 and Jan '03 data) indicates that

5    reactions (1), (2), and (3), and probably (4) and (5), are always kept at "maximum" rate, never completely stopped. These reactions correspond to the low level of electrochemical change occurring at Imin.

While not wishing to be bound by theory, it is believed that the present advantages of the invention are obtained by the following mechanism. An

10   anode typically forms a passive surface layer in a first reaction as an intermediate in the formation of ferrate VI. The passive surface layer is typically formed by the reaction of Fe(0) to $Fe_XO_Y$ (e.g. FeOOH, $Fe_2O_3$, $FeOH_3$, $Fe_eO_4$ ) formed on the anode. The passive layer is a poor conductor or is substantially nonconducting with reference to the conductivity needed for the

15   process. The passive layer typically interferes with the desired reactions by Increasing the voltage required to operate the cell. Accordingly this increases costs by greater use of energy, by higher costs due to the need to build more robust cells to handle the higher voltages and by lower efficiency of conversion to Fe(VI).

20   The reactions are typified and described by the following. In a first reaction, Fe(0) is converted to several higher oxidation species by electrolytic reactions depicted as:

25   $Fe^0 \rightarrow Fe^{II} \rightarrow Fe^{III} \rightarrow Fe^{IV} \rightarrow Fe^V \rightarrow Fe^{VI}$ (soluble product)

Moving to the right, the reactions $Fe^0$ through $Fe^{VI}$ are electrochemical in nature, are driven by the cell voltage across the anode and cathode, and form the final product. Typically, $Fe^{III}$ is a nonconducting, insoluble oxide film

30   that builds up as $Fe_XO_Y$ species over time and eventually makes the process stop, also Fe(IV) to Fe(V) is rate determining step . The inventive apparatus and method allow the process to proceed efficiently over a much longer

10

period of time by preventing the passive layer from growing. This is accomplished by removing the $Fe^{III}$ as it is formed by use of the variable D.C. voltage described herein.

Described below and shown in Figure 1 is an embodiment showing a

5    plant for producing ferrate (VI). The unit would be capable of operating 24 hours per day and 7 days per week using continuous solid product removal (by centrifuge and pressure "plate and frame" filtration). The plant is designed to improve efficiencies so that the ratio Fe (total)/Fe (VI) is decreased toward the ideal ratio of about 1/1. Decreasing this response

10   factor is expected to increase ferrate production in proportion since non Fe (VI) species are believed to involve Fe(VI) decomposition directly, or involve other oxidation states (e.g. Fe(IV), Fe(V)) that give rise to Fe(VI) thereby providing another route to increasing ferrate (VI) production yields. This topic is discussed in more detail below.

15   Referring now to Figure 15, the apparatus shown in this figure can be used to prepare ferrate (VI) according to the invention.


Example 1

Four tests were made. Ferrate(VI) crystals were periodically harvested

20   during every test using a batch filtration process. A known amount of electrolyte was withdrawn from the crystallization tank and vacuum filtered to obtain a cake containing potassium ferrate(VI) micro-fiber crystals with adsorbed electrolyte (solution of water, NaOH, and KOH), and any Fe-containing by-products, especially magnetite. The filtrate was recycled back

25   to the cell. Though this was not a continuous separation, it was effective in keeping the ferrate(VI) production high and preventing ferrate reduction at the cathode or by bimolecular interaction, or by some other means. By keeping the potassium ferrate(VI) concentration low, the reaction leading to the ferrate(VI) salt is enhanced, thus limiting the reduction of ferrate(VI) ions

30   to other undesired iron species.

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This is supported by the data shown in Figure 3, in which the Fe(total)/Fe(VI) ratio doubles when the ferrate(VI) concentration is high (as noted before a lower ratio is better). In Figure 3, the vertical lines indicate a batch filtration event. The sudden rise in current efficiency I eff (CE) at 2750-

5  2800 minutes is attributed to the use of a lower total electrolyte volume/anode area test.


Example 2

This example illustrates the use of a continuous centrifuge.

10  In tests according to the invention and with the batch filtrations described above, removal of ferrate(VI) salt is essential for high production rates. It was demonstrated that external, batch centrifuging of the electrolyte samples provided a simple method of removing the desired product from the electrolyte without significantly changing its chemical and physical properties

15  and, more importantly, without the need of any post-processing as is required with filtration (i.e. leaching and re-crystallization of the ferrate from the wound filter media). However, since that test was external and was not a continuous process, the ferrate concentration in the electrolyte was still permitted to build up and come into contact with the cathode, resulting in

20  reduction and loss of product. Therefore, an in-line centrifuge (or "centrifuge") was tested for continuous crystalline $K_2FeO_4$ product removal

The results show that the in-line separation with a centrifuge was very effective in removing ferrate(VI) crystals from the electrolyte. As observed in tests according to the invention, crystallization occurs at ferrate

25  concentrations above about 4mM at this wt.% KOH concentration and at about 25 C. After each centrifuging procedure, the concentration was decreased to this level verifying this solubility (also verified by absence of particulates in the centrifugate by optical microscopy (OM)), indicating successful and nearly complete removal of ferrate solids from solution. The

30  data shown in Figure 4illustrates this well. The product that resulted was typically 5 wt% ferrate(VI) and physically behaved as a pourable, but thick material. After the product was pressed at 110 psi, thereby pressing out

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more electrolytes from the fine fiber stack, $K_2FeO_4$ content increased to 20 wt.% or more. Note that in Figure 4 that solubility at these conditions is measured as 4-5 mM (filtrate concentration).  T = ± 5 C.  Note increase in current efficiency (%) is only 2% with only occasional harvesting.

5

Example 3

This example illustrates the power supply variable DC waveform and wave properties. A modified sine wave was used. In nearly all cases, the top portion of the waveform was found to be chopped, or flattened. This voltage

10  is defined herein as Vmax. While not wishing to be bound by theory, this observation is (tentatively) interpreted to be due to the reaching of the Fe oxidation potential, thereby effectively reducing internal resistance (increased electron flow by chemical reaction). The oxidation of Fe(0) to Fe(VI) occurs at the higher voltage as seen by purple color formation. By modifying the

15  waveform in this manner and forcing the voltage to remain at this high value for a significant part of the cycle, the production of Fe(VI) may be maximized. This was observed during tests according to the invention . However, Vmin is also important (see discussion herein).

A modified square wave was also tested. This waveform was not

20  entirely square; however, as the amplifier used was not capable of the required fast response time due to the amperage required. The voltage sweep from the minimum to the maximum voltage was therefore substantial, resulting in a waveform more resembling a sine wave chopped on the top and bottom. However, these two waveforms allowed testing the effects of Vmin

25  duty cycle. In this manner it was determined that a modified square waveform resulted in higher current efficiencies for ferrate(VI) production, i.e., Vmin duty cycle needs to be approximately long enough to allow the observed "decay" in voltage due to a second reaction.

30  While not wishing to be bound by theory, it is believed that the present works by the following mechanism as presently understood. In a cell as

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illustrated in figure _____. Current flow at the iron containing anode reduces the iron in the sequence

$$Fe(I)->Fe(II)->Fe(III)->Fe(IV)->Fe(V)->Fe(VI)$$
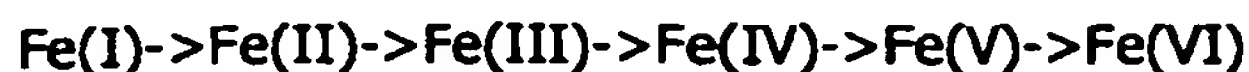
      fast      fast      slow   very slow  fast

5        R1      R2     R3      R4      R5

The reduction reactions have various speeds. Thus the slow reaction R3 and R4 cause a film buildup of of Fe(III) and Fe(IV). Fe(V) is quickly removed due to its fast conversion to Fe(VI). In addition Fe(III) and Fe(IV) are relatively insoluble in the water or the alkaline mixtures used in the

10 generating cell. This film typically interferes with current flow and ferrate production as it gets thicker on the anode. Prior art methods require that production be stopped to remove this film. The present invention provides methods for preventing the buildup of this film during continuous production of ferrate. This is key to efficient large scale production of ferrates and for

15 obtaining high current efficiencies.

    Reduction and limitation of the film to that required for high current efficiency in ferrate production entails the use of a variable direct current or voltage. In contrast prior art methods have used alternating currents and direct currents that do not provide for appropriate reduction of the film.

20     Referring now to Figures 5, 5A, and 11, the present invention uses a variable wave DC voltage that alternates between a maximum voltage at which ferrates are optimally produced and a minimum voltage at which ferrate production is slowed. If one attempts to provide a DC voltage higher than that at which ferrate production is maximum, the voltage will be cut off

25 (while current flow will greatly increase) due to increased ferrate production and be in the form of a flat topped wave. Referring to Figure 5A, the voltage is increased (A) and ferrate is produced and peaks as the voltage increases to V = Vmax, (B). This voltage is maintained for a selected time and then turned off. As a result the current drops as shown in curve C. However the

30 voltage does not drop off in the form of the wave that is applied, rather the drop off is delayed as shown in the three figures by the curve C. Thus instead of a straight drop an applied square wave drops asymptotically to the

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lower voltage of Vmin (F). The voltage then increases again as shown by curve A'.

During the dropoff period it is believed that ferrate production is reduced or ceases, however, the reaction Fe(III) to F(IV) and `Fe(V) continues which reduces the film. After the film has been reduced a selected amount, the voltage is reapplied and the process repeated. Typically the frequency (Peak to Peak) of the direct current pulses is between about 0.01 HZ and 1,000HZ.

On exiting the production cell the soluble Fe(V) and Fe(VI) are quickly sent to a finishing cell to convert substantially all of the Fe(V) to Fe(VI). If this is not done the water soluble Fe(V) may disproportionate and produce 2Fe(V)->Fe(IV) + Fe(VI). The Fe(IV) may then be lost as a coating on surfaces. Another side reaction at the anode surface that must be minimized is Fe(VI) + Fe(0) -> 2Fe(III) (Fe2O3) since this forms a film and passivates the anode.

Temperature control is preferably used to control side reactions and speed the reaction rate. Thus an increase in temperature avoids side reactions with the anode electrode and avoids deposition of byproducts such as $Fe_3O_4$. Preferred temperatures are about 10 C to about 70 C. More preferred are temperatures of about 25C to about 50C, while most preferred are temperatures of about 40C to about 45C. As electrolyte containing Fe(VI) product exits the personnel

When only a screen and no membrane was used, the typical maximum voltage used was 2.8-3.0V. This was limited by the reaction chemistry. However, this voltage was sufficient to drive the reaction and gave high initial current efficiencies.

A lower maximum voltage was also tested (Vmax=1.7V) by dropping the total current to 1/3 of maximum (about 15A) during one test and resulted in elevated current efficiency at long time on stream. It should be noted that low voltages are desirable from an economic standpoint as power costs are

15

proportional to voltage. Therefore, the lower voltage use will result in a significant reduction in energy costs.

The current sweep was typically from 1 to 50 A (the maximum output current allowed by the power supply). However, during one test, the maximum current was decreased to 17 A. This decrease in current resulted in a lower production rate of ferrate(VI). However, since the amount of current passed to the cell was lower, the resulting current efficiency remained the same.

Variations in the frequency were also tested. The frequencies used were 1, 2, 2.5, and 5 Hz. However, under the conditions tested, no clear trends were observed with these variations. The waveform appeared to have a greater impact on current efficiency. For the equipment used and the range of frequencies performed in the tests it appears that for a given waveform with similar voltage characteristics, current efficiency increases with frequency.

For example, using an offset AC signal, a sine wave of 60 Hz with a Vmax of 4.00 V resulted in a current efficiency of 16.79% while a sine wave of 0.1 Hz with a Vmax of 9.04 V resulted in a current efficiency of 0.69%. This high frequency, however, is within the range of the power supply used. Once knowing the teachings of the invention herein, a person skilled in the art will be able to perform routine statistically designed optimization tests to identify the most efficient combination of power supply frequency, current density, waveform, Vmax, and Vmin profile.

The materials are available from the Carus Chemical Company

Effect of KOH Concentration and Addition Time

During tests of the invention, it was observed that stable ferrate(VI) salt crystals can be produced directly during ferrate(VI) production, and obtained in good yield, using a mixture of NaOH and KOH as electrolyte. However, it was also found that KOH causes a reduction in current efficiency compared to NaOH (see also Bouzek and Rousar). Therefore, KOH was added after electrolysis was begun for all tests as ferrate(VI) production was

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very slow if it was added before power up.  After startup, KOH addition results in an initially high current efficiency that decreases drastically over time.  However, in most of the screening test runs, the current efficiency began dropping <u>before</u> the KOH was added indicating that the ferrate(VI)

5    production rate was hindered by some parameter other than $K^+$ concentration.  The screening testing also revealed that isolated sodium ferrate(VI) salt is unstable, a build up in ferrate(VI) concentration in NaOH solution will lead to decomposition and lower current efficiencies.

        The KOH concentration was varied during these tests; utilizing 2, 4,

10   and 8 wt% KOH in the electrolyte.  The lower KOH concentration resulted in higher ferrate yields.  The test on December 19-22 used 2 wt% KOH and resulted in about 6% current efficiency once the KOH was added.  This was a significant increase compared to other results in which 8 wt% KOH was used; after the KOH was added, the current efficiency was 1%.  Furthermore,

15   Figure 4 shows the effect of increasing the KOH concentration from 4 to 8 wt% during the test.  The resulting ferrate(VI) production rate decreases from about 20 to 10 g/day.


Effect of Electrolyte Volume to Anode Are a Parameter

20   However, note that these tests were qualitative in nature and so did not provide optimized %KOH, %NaOH, or K/Na ratio levels.  Such results need to be determined using systematic statistically designed tests so that these parameters are optimized in conjunction with other key process parameters, which includes continuous product as data and by-product prevention (see

25   Section 6.3).  In some large industrial scale electrochemical process, for example, per sulfate/hydrogen peroxide, the ratio of analyte volume to anode surface area is a key design parameter.  Therefore, the effect of electrolyte volume was examined in one experiment.  It was observed that decreasing the volume by half resulted in an increase in an immediate substantial

30   increase in both ferrate(VI) concentration and current efficiency.  This is illustrated in Figure 6 in the 6000-7000 min. data region, 1% to 3%.  Hence, this V electrolyte/anode area ($V_{elect}/A_{anode}$) is also a key parameter.


17

The solid square indicates a plot of current efficiency for each interval between harvesting. The solid diamond indicates a plot for cumulative current efficiency (yield%). The solid diamond indicates a plot of the ratio of total iron to ferrate (VI),  Fe:Fe(VI)

5      It is important to note that in Figure 6 the decrease in electrolyte volume from 17 L to 9 L resulted in an increase in current efficiency (actual interval) from 1.1 to 3.1%. Note that product harvesting was not continuous.


Example 6
10     Screening Testing:  Experimental Data Summary
       The four data tests performed were all carried out with a similar "simplest case" cell configuration; PVDF construction using one iron anode sandwiched between two nickel cathodes providing a total of 866 cm$^2$ of anode surface area.  No Nafion membrane was used, thus allowing low cell
15     voltage and the removal of the second fluid stream and associated plumbing, tank, and pump.  A single electrolyte solution also simplifies the process, and this solution was pumped at about 1.5-1.8 gpm, through the system where it contacted both sides of the iron anode in a parallel flow pattern.  The flow distributor in the base of the cell provided uniform flow rate to both sides of
20     the anode.  Dual power contacts helped provide uniform (top and bottom) electrical current to all the electrodes.  To avoid over dilution of electrolyte, the experiments were begun by pumping about 10L of 45 wt% NaOH solution through the system for approximately 30 min.  The cell was then operated for a known period, approximately 1000 min before adding appropriate amounts
25     of KOH solution in these screening tests, which allowed sufficient time for sodium ferrate(VI), $Na_2FeO_4 \bullet (H_2O)$, to form (note that this period was reduced substantially further later, which avoids $Na_2FeO_4$ crystallization.  The resulting electrolyte volume was between 14-18L with NaOH concentration of about 32 wt% and KOH concentration of 2, 4, or 8 wt%.  Filtration was
30     performed by extracting a volume of electrolyte (normally 1 gallon) from the crystallization tank discharge valve and performing a 1 atm vacuum Brichner funnel filtration.

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An in-line centrifuge (contrafuge) was also tested successfully for solids separation. When centrifuging, a peristaltic pump was used to transfer electrolyte from the crystallization tank to the centrifuge at a flow rate of
5   100mL/min. The centrifuge was operated at various rpms over the whole range available to the device (6000-10,000 rpm), and it was determined to not greatly affect the separation. Therefore, the product (and by-product magnetite crystals) and "sea urchins" crystals, easily recovered by centrifugation. For example, after 1hr of centrifuging, the separation process
10  was stopped and the product examined. The product from the centrifuge was typically about 5 wt% ferrate; this was increased to about 20 wt% by pressure filtering this cake to 100-130 psi, making a solid wafer "tablet". Throughout the test, ferrate(VI) concentration in solution was determined by UV-Vis as described in previous reports.

15     The experimental conditions and initial current efficiencies for the December tests are included in Table 1. In each test, the waveform was altered over a limited range to determine any effect on ferrate(VI) production (see later for Vmin duty cycle adjustment testing).

       Although the waveform was varied during each experiment, the
20  waveform and voltage characteristics listed here are the initial settings only and are valid for the listed current efficiencies. These are not optimized parameter values. Note the increase in current efficiency with 1.9% KOH in the electrolyte relative to higher levels.

25  Table 1: Experimental Conditions and Results for Four Tests

| Run Start Date | Waveform | Freq (Hz) | Vmax (V) | Vmin (V) | Initial Current Efficiency (%) | KOH wt% | Current Efficiency (%) After KOH Addition |
|---|---|---|---|---|---|---|---|
| Dec. 2 | Square (#1) | 1.0 | 3.40 | 1.60 | 10.8 | 4 | 1.5 |
| Dec. 8 | Sine (#2) | 1.0 | 3.00 | 1.32 | 9.2 | 8 | 0 |
| Dec. 15 | Sine (flat top) (#3) | 2.0 | 3.08 | 1.72 | 10.0 | 8.9 | 1.0 |
| Dec. 19 | Sine (flat top) (#4) | 2.5 | 2.88 | 1.72 | 13.4 | 1.9 | 6.4 |

19

Sample 2 Summary

The ferrate concentrations measured during this test are presented in
Figure 6 and Table 1. As seen in the table and Figure 6, the current efficiency
was initially over 10% (in NaOH solution) but decreased with time. In the 32
5    wt% NaOH/4 wt% KOH solution, the current efficiency was about 1.5% to
about 2%. With an increase in KOH concentration at 4000 min on stream,
the current efficiency decreased slightly, as did the rate of ferrate(VI)
production. Although the Vmax was altered at 375 min time on stream from
3.40 V to 3.00 V, this did not result in any noticeable change in ferrate
10   production rate, indicating that the same production rate is possible at lower
power.

Sample 8 Summary

This test utilized four different waveforms as described in Table 2. The
15   addition of KOH to the system was done in conjunction with the change in
waveform from a sine (single point Vmax) to a sine with flat top. This change
correlated with a drastic drop in current efficiency as seen in Figure 6.

20

Table 2

25    Waveforms Used in the Sample 8 Tests

| Time on Stream (min) | Waveform Description | Waveform Ref. |
|---|---|---|
| 0-1161 | 1hz sine, Vmin=1.32, Vmax=3, Imax=54, Imin=0.5 | 6.2..2.1 |
| 1161-2885 | 2hz sine with flat top 220ms, Imax=54, Imin=14 | 6.2.2.2 |
| 2885-3850 | 2hz square with flat top 240ms, 20ms slew up and down, Imax=51, Imin=3 | 6.2.2.3 |
| 3850-6792 | 2hz square with flat top 400ms, 100ms slew up and down combined, Imax=55, Imin=33 | 6.2.2.4 |

20

The third and fourth waveforms (square waves) correlate with increased current efficiencies as seen in Figure 6 and with ferrate production rates as seen in Figure 7.

5          It should be noted that the ferrate concentrations are greater than these because the solid products extracted from the electrolyte during the filtration and centrifuging steps were not included in the data presented in Figure 7. The production rate data, however, shows a marked decrease once the KOH has been added. However, the ferrate production rate increases

10    again when the waveform is modified to a square wave (i.e., a Vmin duty cycle, as well as the Vmax duty cycle). Also, during the last filtering step (about 6650 min on stream), the electrolyte was decreased to half its original volume (Figure 6). This decrease in volume resulted in an increase in both production rate and current efficiency. In some large industrial scale

15    electrochemical process, for example, per sulfate/hydrogen peroxide, the ratio of anolyte volume to anode surface area is a key design parameter.

Sample 15 Summary

          During this test, separation of solids was performed by frequent

20    filtration only; the centrifuge was not used. The waveforms used in this test are described in Table 3. A sine wave with a flat top was used throughout most of this test

25          Table 3: Waveforms Used for Sample 15

| Time on Stream (min) | Waveform Description |
| --- | --- |
| 0-47 | 2hz sine wave, unmodified, Vmax=3.08, Vmin=1.72, Imax=45, Imin=8 |
| 47-922 | 2hz sine wave, modified WITH FLAT TOP (170ms) at 50A, Vmax=3.08, Vmin=1.72, Imax=50, Imin=8 |
| 922-1819 | 2.5hz sine wave, modified WITH FLAT TOP (160ms) at 48.5A, Vmax=2.88, Vmin=1.76, Imax=48.5, Imin=13.5 |
| 1819-2385 | 1Hz square with 500ms top at V=3.08, Imax=50, Vmin=1.72, Imin=1.5, 80ms bottom trough |

21

Figure 8 shows a graph of ferrate concentration on the left vertical axis and Ferrate Production Rate on the right vertical axis, versus Time in minutes on the horizontal axis. Test data are for Sample 15. Sample 15 tests resulted in initially high current efficiencies (about 10%) that decreased to 1-2% by

5    1000-1500 min (Figure 8). The 1 Hz square wave used at the end of the run resulted in decreased ferrate concentration in solution as seen in Figure 8. However, at the end of the run, the current efficiency was jumped from 0.11 to 7.16% as did the ferrate production rate. The ferrate concentration shown in Figure 8 is, again, only the solution concentration and does not include

10   ferrate solids separated out during the test run.


Sample 19

     This sample used 1.92 wt% KOH, added after only 80 min after start-up. At this time, the waveform was also changed from a sine wave to a sine

15   wave with a flat top. Table 4 describes the waveforms used for this sample.


20                         Table 4: Waveforms Used in Sample 19

| Run Time (min) | Waveform Description |
|---|---|
| 0-75 | sine wave, 2.5Hz Imin=3A, Imax=33A, Vmax=2.32, Vmin=1.48 |
| 75-3440 | sine wave 2.5Hz, with flat top 120ms, duty cycle sine shaped bottom, Imin=12, Imax=47, Vmax=2.88, Vmin=1.72 |
| 3441-4211 | sine wave 5Hz, with flat top 100ms, sine shaped bottom, Imin=12.5, Imax=17.5, Vmax=2.44, Vmin=1.80 |


     Figure 9 is a graph showing Ferrate production Rate (g/day) in the left

25   vertical column; and Current Efficiency (%) and Total iron/Iron(VI) ration (Fe:Fe(VI)) on the right vertical scale; versus Time (minutes) on the horizontal scale. For most of the run, a sine wave with a flat top was used,


                                    22

resulting in a current efficiency of about 6.5%. The cause of the dip in efficiency and production rate between 500 and 1250 minutes is unknown, but believed to be caused a build up of ferrate in solution. This result was interpreted to indicate, and later proven during parameter validation testing,

5  that continuous product removal is important to prevent product reduction to by-products in the cell when they are recirculated. Therefore, separation of solids should have been performed earlier in the test run. Near the end of the test run, the frequency of the wave was increased and the current decreased. The lower current being supplied to the cell resulted in a lower

10  ferrate production rate, but a constant current efficiency. This result verified earlier results for undivided cells, which indicated ferrate production rate is proportional to current if all else is held constant (at least at this general current density).

15  Continuing the results for Sample 19, the concentration of ferrate(VI) in solution is presented in Figure 10 on the left vertical axis in mM and the production rate in g/day on the right vertical axis versus Time in minutes on the horizontal axis. As seen in the figure, the concentration reaches high levels during the initial stage of the run, even after KOH has been added.

20  The low concentration of KOH (about 2 wt.%) results in a high current efficiency throughout the run compared to the current efficiency obtain in solutions containing 4-8 wt% KOH (Figure 10). All of the various separation processes used in this run worked well in removing the solid ferrate from the electrolyte. After 1500 min on stream, the filtration and centrifuging resulted

25  in nearly complete removal of solids as indicated by the resulting ferrate concentration of about 4mM in the electrolyte at these conditions. As mentioned before, this is near the saturation point for ferrate(VI) in the NaOH/KOH electrolyte. However, the sharp increases in ferrate(VI) concentration and rate at the beginning and middle of the run (see Figure

30  10) again indicates that a continuous solids separation process should be employed. Importantly, the frequent separations result in good agreement between the 505 and 785nm spectral peaks in the UV-Vis spectra of the

23

ferrate samples, indicating a high purity of Fe(VI) in the samples (i.e., low level of magnetite and FeOOH called by-products).

Sample 119

5      The test performed for Sample 119 was used to validate the findings of the previous Sample 2, 3, 6, 8, 15, and 19 runs. The results from these tests indicated that following modifications and parameters were probably key to enhanced electrical current efficiency, product purity, and continuous operation.

10   1. Decreased electrolyte volume/ anode surface area ratio. This parameter was adjusted using two methods. First, a second iron anode was installed in a cell, increasing the total surface area from 866 $cm^2$ to 1732 $cm^2$, and secondly, the total volume of electrolyte was decreased.

2. A waveform with both a flat top and bottom was employed. The duty
15   cycle was optimized in regard to current efficiency. A possible mechanism for this effect is that the tailing out and flattening of the waveform at Vmin limits the build up of passivating film thickness, and perhaps reaction intermediates formed at the higher voltage.

3. KOH introduced early in the run; a short time after electrolysis is begun.
20   Also, the effect of the low KOH concentration utilized in the Sample 19 run was to be verified.

4. A thin open screen (not a membrane) to separate the anode and cathode compartments. The exiting electrolytes were split and a valve was added to the exiting catholyte line to reduce flow across the cathode. This was done to
25   minimize/prevent hydrogen from the cathode from contacting the ferrate(VI) produced in the anodic compartment, and to limit $FeO_4^=$ access to the cathode. By limiting the reduction of ferrate(VI) in the system, the overall yield should increase.

5. Reduced lower current density. This was obtained by both increasing the
30   anode surface area in the electrolytic cell. Current density could be decreased further by reducing the total current through the cell, but this was not tried in these tests to keep ferrate(VI) production rate as high a possible. Literature

24

data indicates that current yield reaches a maximum around 3-4 mA/cm$^2$ for short run times. The tests according to the invention were typically run around 57 mA/cm$^2$ (with one experiment at ~20 mA/cm$^2$), where literature data indicates a low in current yield.

5    6. Literature data also indicates that higher temperature (~40-50°C) results in increased current efficiencies, approximately three times greater than those obtained at 20°C. However, previous work and the same literature has indicated that ferrate(VI) decomposes at these elevated temperatures resulting in a high total iron to iron(VI) ratio, and so most work has been

10   done at 25°C (in 2002). Therefore, the electrolyte was heated to 50°C before entering the cell and then immediately cooled back down to 20°C on exiting. The temperature control logic was then to maximize Fe(VI) production rate while limiting ferrate(VI) decomposition, and facilitate crystallization yield.

15   Sample 114 Summary

         The tests were performed using a modified cell configuration; two iron anodes placed between three nickel cathodes. A plastic screen to inhibit contact between ferrate and the cathodes was used. A single electrolyte solution was pumped through the system and contacted both the anodes and

20   cathodes. The experiments were begun by pumping 10.8L of 43 wt% NaOH solution through the system for approximately 60min before adding appropriate amounts of KOH solution. The resulting electrolyte volume was 11.0L. Throughout the test run, the NaOH concentration was 42-45 wt% and the KOH concentration was 0.8-1.3 wt%. The electrolyte was heated to 43°C

25   before entering the electrolyser and cooled to 37°C in the surge tank. Although the ideal temperatures would be 50 and 20°C, respectively, these values were not attainable with the plastic heat exchange tubing, being used to avoid ferrate(VI) contamination/destabilization, for the cooling (stainless steel did appear to work well for the heating). Therefore stainless steel was

30   demonstrated for use in continuous ferrate(VI) production for some embodiments. An in-line centrifuge was used to continuously separate solids from the electrolyte. It was soon discovered, however, that the use of the

25

centrifuge required a larger volume of electrolyte. Therefore, additional electrolyte was added to the system at 390 minutes, bringing the total volume to 17.8L. The in-line centrifuge was then run continuously to remove solids from the electrolyte stream. The resulting centrifugate was about 1% solids,

5 as needed to separate the product from the electrolyte so that the electrolyte can be immediately recycled. The slurry then was filtered to produce a high percent active product, the filtrate from which is added back to the process as viable electrolyte. It was later discovered that this centrifuge was plugged with solids, indicating rapid and good solid/liquid separation was occurring

10 and therefore the need to reduce the weir size in the device to allow the slurry to exit the unit without excessive caking. Such weir size determination is within the skill of the art. Filtration was then performed by tapping 2-4 L volume of electrolyte from the crystallization/surge tank exit line and performing a vacuum filtration as was done during the Sample 2, runs but

15 this time as continuously as possible. The product from the filtration step was typically 9 wt% potassium ferrate(VI). Some earlier pressure filtration tests indicated that the percent active was readily increased to > 20% by this means. This mechanism is believed to be because the micro needle crystals need to be under pressure (e.g. compression) to reduce inter-crystal void

20 volume space to rid the crystals of a film or thick coating of the viscous electrolyte. Since such crystals often "spring back", the liquid needs to be removed while the crystals are still under pressure, i.e. in a compressed state. This effect is seen as a typical key criterion to the production of a product of high percent active (> 10%).

25 The electrolyte volume was decreased to 9.2 L at 1654 min to validate the observation made in earlier tests that low electrolyte volume results in an increased current efficiency. Throughout the run, ferrate(VI) concentration in solution was determined by UV-Vis as described in previous reports using 32% NaOH to dissolve the product for the analysis.

30 The waveform used in this experiment was a square wave of 1Hz; the maximum and minimum voltages were 2.20 and 1.26V, and the maximum and minimum current were 56 and 0.4A, respectively. Hence the power level

26

was only about 123 watts, i.e. small. The waveform was captured with a scopemeter (Figure 6.9). Though the waveform of the power supply is a square wave, tailing was observed during the down, and a little on the up, sweeps. This exponential voltage drop is an indication that some chemical

5    change is occurring during the down sweep, i.e. that the cell is behaving as a electrochemcial cell during this period and as an electrolytic cell during the plateau region. While not wishing to be bound by theory, this result is tentatively interpreted to be an indication that the oxide film might be reacting (thinning) in the downward sweep to produce soluble Fe forms (e.g.

10   Fe(V) or Fe(VI) or Fe(II)), which all thin the oxide layer, thereby preventing its thickening, which would lead to passivation. The resulting cell current density was 32mA/cm$^2$ at Vmax.

In using these new production settings for the key process parameters,

15   as determined during the earlier tests, the current efficiency and production rate were observed to increase substantially over previous trials, even after the startup period. In addition the current efficiency was essentially constant. From the total amount of ferrate(VI) produced (included in Figure 12, the production rate during this 4500 min experiment was calculated as 64.1g/day

20   (0.14 lb/day), . The current efficiency versus time (both interval basis and running average) is included in Figure 12. It is important to note that Figure 12 shows a substantial increase in current efficiency over the previous tests. Though previous tests all had high current efficiencies at start-up (see Table - 1), however these values always decreased rapidly with time on stream.

25   Therefore the combination of waveform, cell configuration, continuous product removal, temperature control, low electrolyte volume, and low wt% KOH, used in the present test resulted in a high current efficiency (~28%) that was sustained throughout the run indicating that these parameters were under control and that all the parameters needed to control current efficiency

30   are being controlled. Looking at the fluctuations in the calculated current efficiencies throughout the run gives additional information. In particular, during overnight operations where solids separation was not performed, the

27

efficiency invariably decreased. However, from 2500-3000 minutes, when filtration was performed at a high frequency, the values were quite stable, indicating the importance of solids separation in current efficiency. This is further evidenced in Figure 13 where the 785 and 505 nm UV-Vis peaks for

5 the electrolyte samples are compared. Any deviation in the two measurements indicates the presence of unwanted iron by-products. Midway through the run, when filtration was performed frequently and the electrolyte volume was low, the agreement between the two measurements was good. However, even at this point, when agreement between the 785

10 and 505 nm peak was good, thus indicating a low concentration of other iron species, the ratio of total iron to iron(VI) was quite high, ranging from 2.5-3.5 After the process was shut down, the cell was disassembled and the electrodes examined. A large amount of material, apparently dendritic magnetite, had accumulated loosely on the bottom portions of the cathodes.

15 In previous experiments, a thin layer of dendritic material was observed on the cathodes after shutdown, with a concurrent amount of material flowing in the electrolyte solution. In this run, the dendritic material was not observed in the solution and appeared to be trapped in the cathode compartments, perhaps because of the slow flow rate in the cathodic compartment relative to

20 the anodic compartment made possible by the valve in the catholyte exit line and the presence of the screens in the cell. The presence of this material on the cathodes provides evidence that this magnetite is indeed formed in the cathode, probably from ferrate(VI), as suspected, and validates the concept of preventing iron species from entering the cathode compartment and the

25 value of using the slow catholyte flow /screen technique to control its formation. Presumably, these solids could be removed by opening the catholyte valve to allow the magnetite to flow to the filter (valving in the filter for the time needed), which allows its removal from the cell

Continuous centrifugation was found to be effective, even at low G

30 force, for rapidly and completely separating potassium ferrate(VI) crystals from the electrolyte, thereby regenerating the electrolyte for recycle. Then batch filtration of the centrifuge cake, or slurry for continuous processing, was

28

used to finally isolate a high percent active product, up to > 20%. The results show that the centrifuge was extremely effective in removing ferrate solids from the electrolyte. The continuous removal of ferrate(VI) solids from the system is important in preventing the decomposition of product by

5   recirculating it to the cell; thereby forming reduced iron species (magnetite and ferric oxyhydroxide colloid). It was demonstrated that these by-products could also be removed from the electrolyte by occasional filtration if needed.

The results of current efficiency enhancements confirmed that, when the total electrolyte volume was decreased, the current efficiency increased,

10  indicating the electrolyte volume/anode area to be an important parameter. This result was verified (see below). When the power supply waveform was adjusted to a flat Vmin, versus the normal single-point Vmin, the electrical current efficiency (%$I_{eff}$ or CE) was seen to increase markedly. This setting was verified during additional testing as well. It was observed that using a

15  waveform with a flat top *and* bottom resulted in good current efficiencies. These results were interpreted mechanistically as indicating that Vmax builds ferrate(VI) and oxide film from the iron metal, while Vmin depletes oxide film by forming ferrate(VI) (and perhaps Ferrate(V)), thereby preventing the buildup of a passivating layer of oxide (produced in a non-variable DC

20  current). The sample data set also suggested that increased current efficiency can be obtained with low (2 wt%) KOH concentration.

These findings were incorporated into the Sample 114 test. The objective of this test was to validate the key findings from the earlier runs and to demonstrate that increased current efficiency can be obtained and held

25  during a run. The parameters included low electrolyte volume/anode area, continuous solids separation (by centrifugation or filtration), decreased current density (by doubling anode surface area), separation of anode and cathode compartments using a screen instead of a membrane, and use of a square waveform (i.e. Vmax and Vmin both flat), and low wt% KOH. These

30  adjustments resulted in high current efficiency that was sustained throughout the entire run; efficiency was ~28% over 4438 minutes (>3days) at 2.20V. This is a major breakthrough. Preliminary engineering assessments indicated

29

a current efficiency of 25% or greater at 3.2-4V would result in a ferrate manufacturing cost of $0.48/lb and represent an economically viable process. What is more, these conditions have not yet been optimized. For example, further improvement in the current efficiency may be obtained by 24/7 solids

5    separation (using an in-line continuous centrifuge that is sized for the production cell), lower crystallizer temperature, optimized current density, etc. Another important result is that metals, such as nickel and stainless steel can be used at certain points in the process (cathode and heat exchanger elements respectively) without apparent detriment to the stability of the

10   ferrate(VI) product. Also, the observations illustrate that the amount of magnetite produced to very low levels by the new design for the cell internals.

Flow distributors are preferred in the anolyte compartment. This will force better contact between reaction intermediates in solution, namely

15   $Fe(IV)$, $Fe(V)$, and $Fe(II)(OH)_4^{2-}$, and the anode to produce $Fe(VI)$.

The screens used to separate the anode and cathode must allow electrolyte and water to pass but inhibit or prevent iron species and hydrogen gas from transferring between the anode and cathode compartments. A membrane is not preferred because of the increased resistance; rather, the

20   barrier should be based on size exclusion to prevent the large, six-coordinated iron species from migrating to the cathode compartment. An additional catholyte stream may be used to further inhibit the reduction of ferrate by hydrogen.

Optimization of the temperature controls to obtain the desired

25   temperature of about 50°C into the cell and about 20°C throughout the remainder of the system. This will further increase current efficiency and crystallization. An in-line, continuous, solids separation process that is optimized for the production of ferrate us preferred over a labor-intensive batch filtration. The latest tests indicate the extreme importance in

30   continuous solids removal to both current efficiency and inhibition of by-product formation and/or decomposition of $Fe(VI)$.

30

These changes have been illustrated in a process schematic for one embodiment of the invention shown in Figure 15. The use of screens to separate the cathodic and anodic compartments requires in one embodiment that separate anolyte and catholyte solutions be used, with the corresponding

5    piping and pumps. An in-line, continuous centrifuge (CINC on the schematic) and a filter have been added for continuous separation of solids from the anolyte stream.

The results reported show that the electrical current efficiency was held at economic levels for substantial periods with clear information on which

10   parameters are most critical and how they need to be controlled to achieve good electrical current efficiency, and centrifugation with pressure filtration, both at mild conditions, readily provides a means to isolate a solid product which appears suitable for preparing commercially viable product forms, for example tablets. Important, yet easily controlled, process parameters were

15   found to be key.

The following are test procedures are useful for determining the proper operation of the apparatus in the production of ferrate(VI).

20   Determination of Ferrate(VI) ion Concentration in aqueous sodium and potassium hydroxides by UV-VIS

Determination of Fe(VI) as $FeO_4^{2-}$ ion is the most critical quantitative analysis for keeping the cells in proper operating condition and at high current efficiencies. If the spectra is not interpreted correctly, errors as high as 300%

25   are possible. In addition, the presence of ferrate(III) may be interpreted as additional ferrate(VI).

Procedure

1.    Set up a UV-VIS capable of a wavelength scan, to scan between 450-

30   850nm.

31

2.      Decide on what size quartz cell to use. If the concentration is thought to be higher than 0.01M, then it is recommended that one uses a 1.0mm cell, anything below that, a 1.00cm cell is appropriate.

3.      Check the set of quartz cells, blank and sample, to make sure they
5   match exactly between the range of wavelengths using HPDI water. Run the baseline with the blank cell using HPDI water

4.      Dilute the sample between 3-10x with 32-34% NaOH every time to make sure any crystals in the sample dissolve. Check with optical microscope, if unsure.  Mix well.  Sample should have a nice purple color with no visible
10  particles floating in solution.  Make sure that your total volume is at least 2.50 ml for 1.00 cm cell and 1.00 ml for the 1.0mm cell.

5.      Test diluted sample at specified wavelengths and record spectra to file. 785 nm peak and 505 nm peaks should have values within 0.100 and 1.200 absorbance units, if not, re-dilute another sample with a different dilution
15  factor that corresponds to higher or lower absorbance values depending on the initial results

6.      Spectra should look like Figure 38, see troubleshooting section if peak shape does not match

7.      Use Beer's Law, A=e*B*C, to calculate concentration.  Use the 505nm
20  absorbance value (A) with 1103 as molar absorptivity (e) value, use cm for path length (B) units and concentration(C) will be in molarity (M).  Do the same for 785nm and an "e" value of 379.  Make sure to multiply the result by the dilution factor.  If the resulting concentrations do not match to within 0.0005M or 0.5mM, see troubleshooting section.

25

Troubleshooting Guide

1.      Make sure that the sample is mixed well enough, that the quartz cell and the detector are clean and whether the sample has a lot of microbubbles trapped in solution.  If present, try to tap the microbubbles to the top or let
30  settle for one minute before running analysis.

2.      The diluted sample may be decomposing during analysis ( i.e. rust color in cell after analysis).  If not sure, set the UV-VIS to real time single

32

wavelength monitoring at either 785 nm or 505 nm. Re-dilute another sample with 32-34% NaOH, mix well, and place into UV-VIS. If the absorbance values are changing faster than 0.003 every minute then it will be necessary to extrapolate the absorbance value back to time zero using the

5     single wavelength function (Use the 505 nm wavelength for this procedure).

This is an indication that something is seriously wrong with the condition of the electrolyzer and should be checked immediately, especially if the ABS values are changing fast (0.001 every few seconds).

3.     If peak separation is still occurring after the above steps are tested

10     then there is another iron species contaminating your sample. The easiest way to get around this is by centrifuging the diluted sample for three (3) minutes at maximum speed. Then use a transfer pipette to remove the top layer of electrolyte making sure not to shake or stir the solids back into solution.

15     4.     If all else fails, filtering the diluted electrolyte with a compatible syringe filter with 5 um porosity or less should be used before analysis.

5.     If nothing works then something is seriously wrong wither with the running condition of the electrolyzer or the electrolyte has been contaminated and needs to be replaced.

20

Determination of Total Iron Concentration by UVIS Analysis

The UVVIS method for total iron determination is an extremely useful and cheap analysis and was verified by ICP-MS analysis. If done correctly, analysis will be accurate to within 1% .

25     1.     Set up a UV-VIS capable of a wavelength scan, to scan between 200-500 nm.

2.     Using the 1.00 cm quartz cell set, test blank and sample cells with HPDI water, to make sure they match exactly between the range of wavelengths. Test the baseline with the blank cell using HPDI water.

30     3.     Begin by diluting the sample with reagent grade 6N HCl by a factor of 50-100x. Solution should turn a faint yellow color and there should be no particulate floating in the sample

33

4.	Scan the sample between the specified wavelengths and save to disk. The spectra should look like Figure 39.

5.	Using the 358 nm ABS value, calculate the concentration of iron in parts per million (ppm) by dividing the $ABS_{358}$ by 0.0551 and multiplying by the dilution factor. In order for the resulting value to be accurate, the diluted concentration must be with in 1-10 ppm. Check this by not multiplying by the dilution factor. If the concentration is too high or low, then dilute another sample with different dilution factor that corresponds to higher or lower absorbance values depending on the initial results.

Filter Leach method for weight determination of Ferrate(VI) salts accumulated on Teflon and Spun PP Cylindrical Filters

This method is useful for determinations where ferrate is removed bu filters. Using an inline filter for removing Ferrate(VI) solid from electrolyte flow streams requires processing so that the total amount of accumulated iron(VI) and total iron can be found and a mass and energy balance can be constructed around the overall electrolytic Fe(VI) process.

1.	Once a filter has been successfully loaded with iron(VI) and removed from the system, allow to drain for several minutes to remove any excess electrolyte, under N2 atmosphere if possible.  Place any collected liquids back into the surge tank.

2.	Make up 3-4L of 6M KOH and cool to about 4.0C.  The final volume is not important as long as the leaching unit (see figure A.3.3.1) has enough liquid so the pump does not cavitate.  Record the exact final volume of 6M KOH.

3.	Load filter into leaching unit and pass 6M KOH thorough it for 5 minutes.

4.	Immediately analyze leachate for Fe(VI) using procedure described in Determination of Ferrate(VI) ion Concentration above.  Dilution may be necessary to reduce ABS values.

34

5. Back calculate total amount of ferrate(VI) in grams by multiplying concentration by total leach volume and molecular weight of ferrate(VI). Some values are given for reference in Table 5.

5      Table 5.

| Fe(VI) salt type | MW |
|---|---|
| Sodium | 165.822 |
| Potassium | 198.039 |
| FeO42- only | 119.843 |

10      While the forms of the invention herein disclosed constitute presently preferred embodiments, many others are possible. It is not intended herein to mention all of the possible equivalent forms or ramifications of the invention. It is to be understood that the terms used herein are merely descriptive, rather than limiting, and that various changes may be made

15      without departing from the spirit of the scope of the invention.

35

APPARATUS FOR PRODUCING FERRATE (VI) AND METHOD FOR PRODUCING
SAME

## CLAIMS

We claim:

Typical embodiments of the invention and claims include:

1. All novel apparatus disclosed in the specification, drawings, and abstract.


2. All novel methods disclosed in the specification, drawings, and abstract.


3. All novel uses disclosed in the specification, drawings, and abstract.


4. All novel articles of manufacture disclosed in the specification, drawings, and abstract.


5. All novel compositions disclosed in the specification, drawings, and abstract.

APPARATUS FOR PRODUCING FERRATE (VI) AND METHOD FOR PRODUCING
SAME

## ABSTRACT

Apparatus for producing ferrate with an electrochemical cell including .
a container a cathode chamber within said container; an anode chamber
within said container and adjacent to the cathode chamber; a separator that
separates said anode chamber from said cathode chamber; and a power
supply for generating pulsating direct current and voltage for application to
said cathode and said anode. Typically the variable direct current voltage
across said anode and cathode, is applied between a maximum voltage,
Vmax, is applied, and a minimum voltage, Vmin is applied across said cathode
and anode, where Vmin is above 0 Volts and is preferably at least the voltage
required to substantially overcome passivation at the anode

Title: Apparatus for Producing Ferrate (VI) and Method for
 Producing Same
Inventors: Monzyk, Bruce F., et al.
Attorney: Klaus H. Wiesmann, 614-424-6589
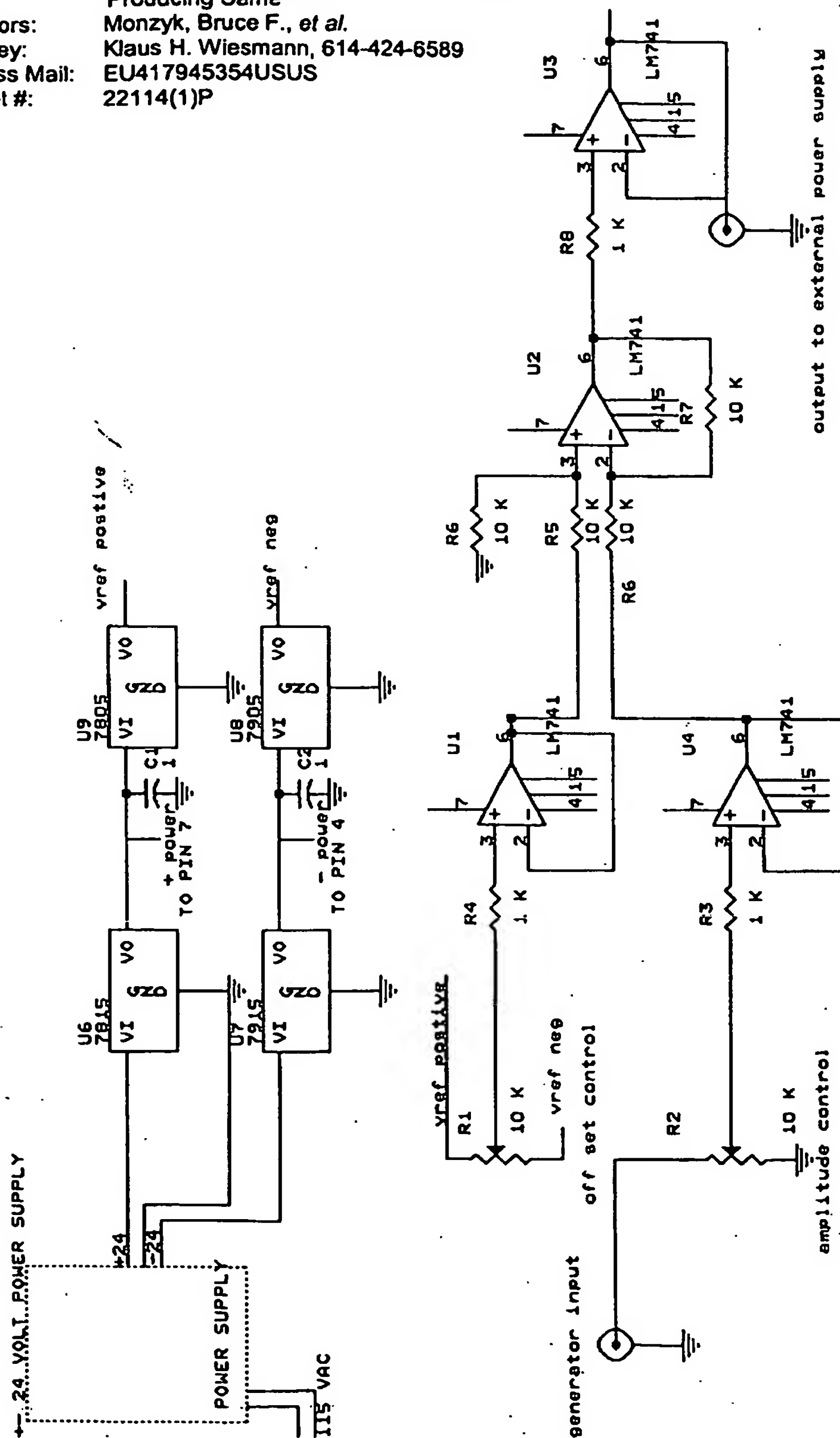Express Mail: EU417945354USUS
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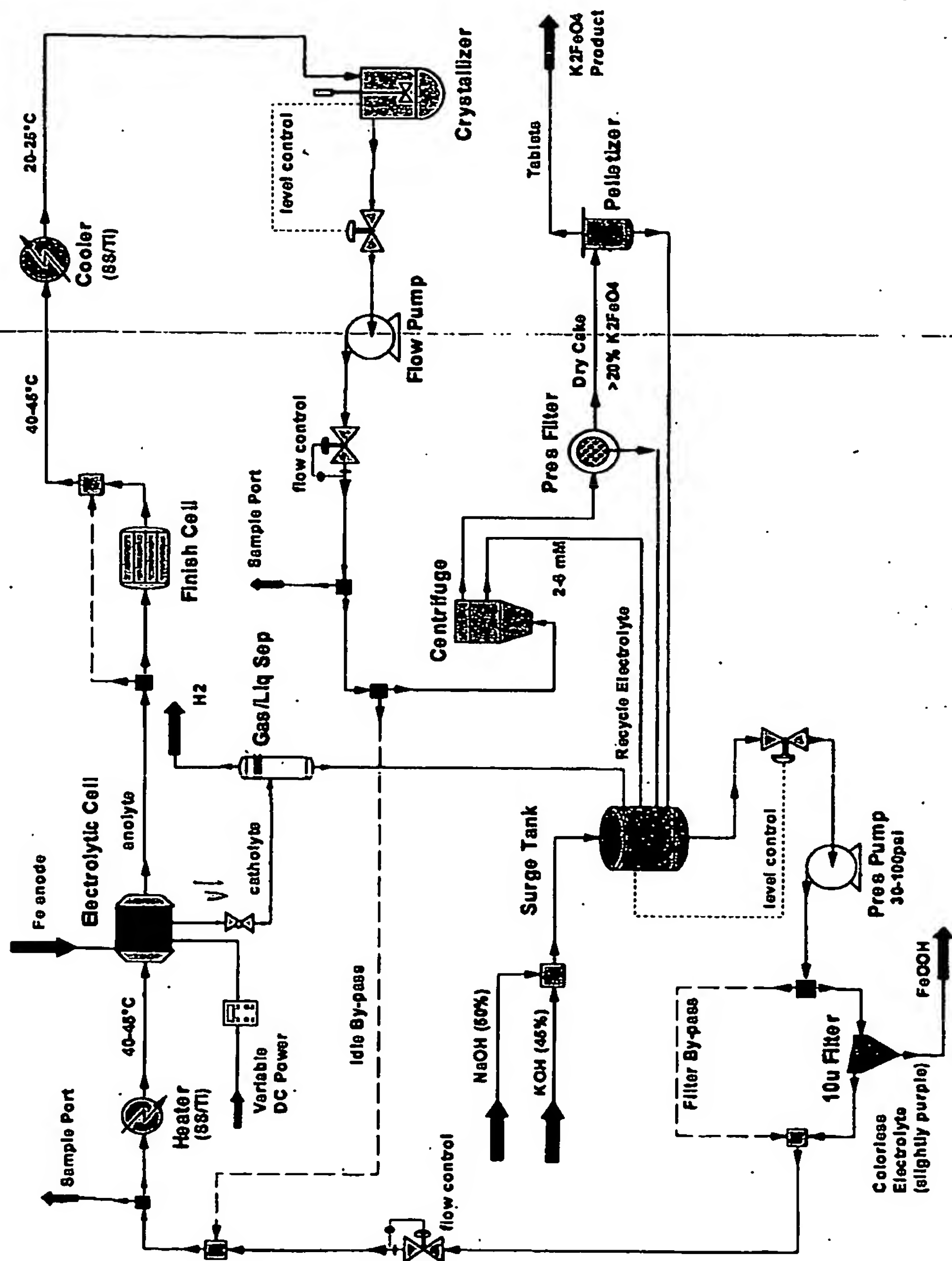
FIGURE 1

# OVERALL POTASSIUM FERRATE(VI) PRODUCTION PROCESS CONCEPT

Power (2.2V x 55A = 120 W)

CELL

ANOLYTE (0.18 gal/min)

40-45C to 20-25C

CRYSTAL- LIZER & SURGE

[Fe(VI)]tot = 20 mM (2mM in solution 18 mM as K2FeO4(xl))

SLURRY (0.18 gal/min)

CATHOLYTE 0.02 gal/min

Make-up KOH, NaOH &/or H2O as electrolyte solution (1.5 L PER 48 HRS)

FILTRATE & SURGE

H2

FILTRATE (0.18 gal/min) (2 mM Fe(VI))

S/L SEPARATION (10u FILTRATION)

POTASSIUM FERRATE(VI) PRODUCT (50g/ hr, 34 mL/hr):
* 9% K2FeO4
*5% (max) other Fe by- products
*84% lectrolyte

TOTAL VOLUME OF ELECTROLYTE ON CIRCUIT = 12 L:
*4L in piping and pumps
*4L in crystalizer
*4L in Filtration

PUMP (0.2 gal/min)

20-25C to 40-45C

Electrolyte (43% NaOH 5% KOH, 2 mM Fe(VI))
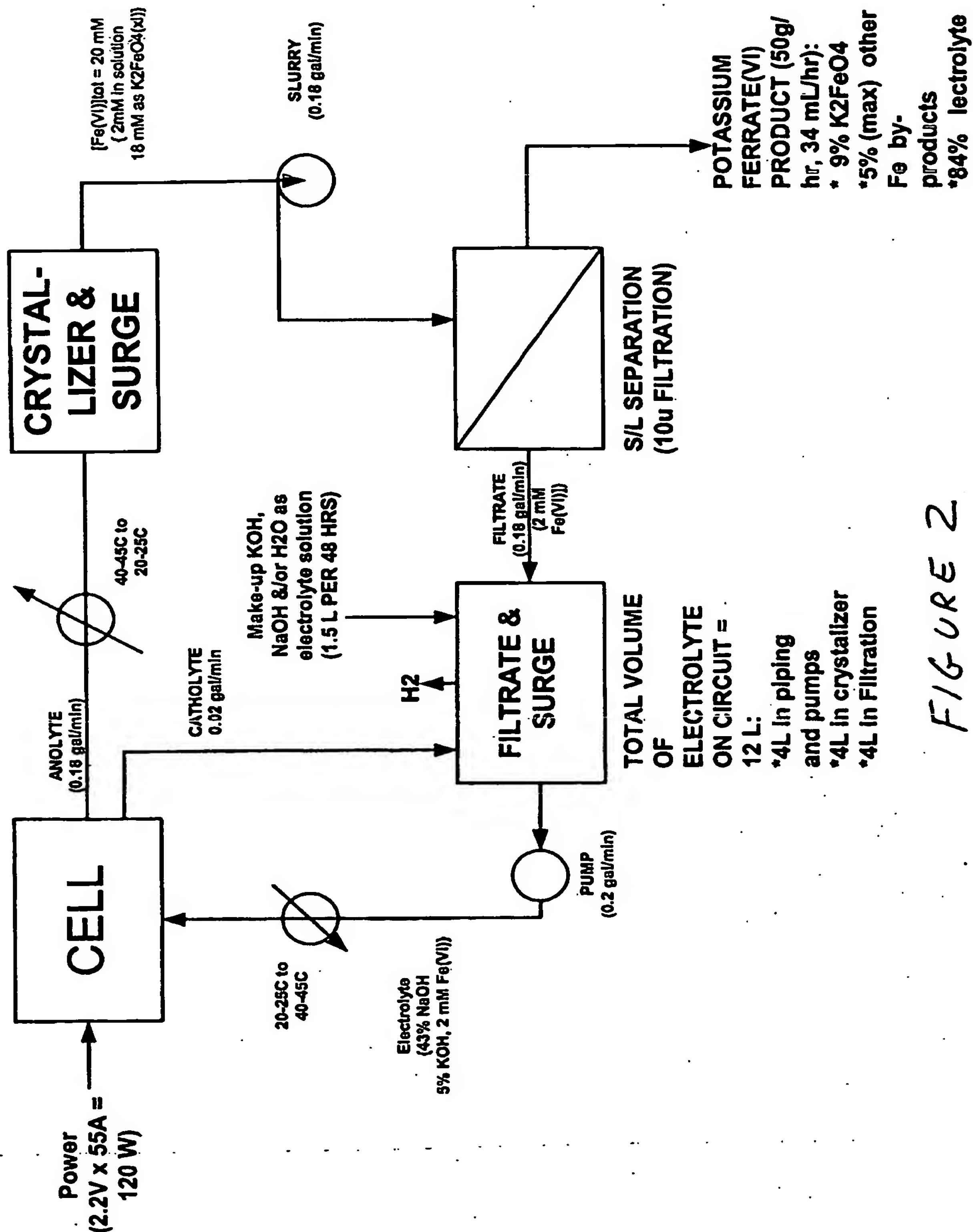
FIGURE 2

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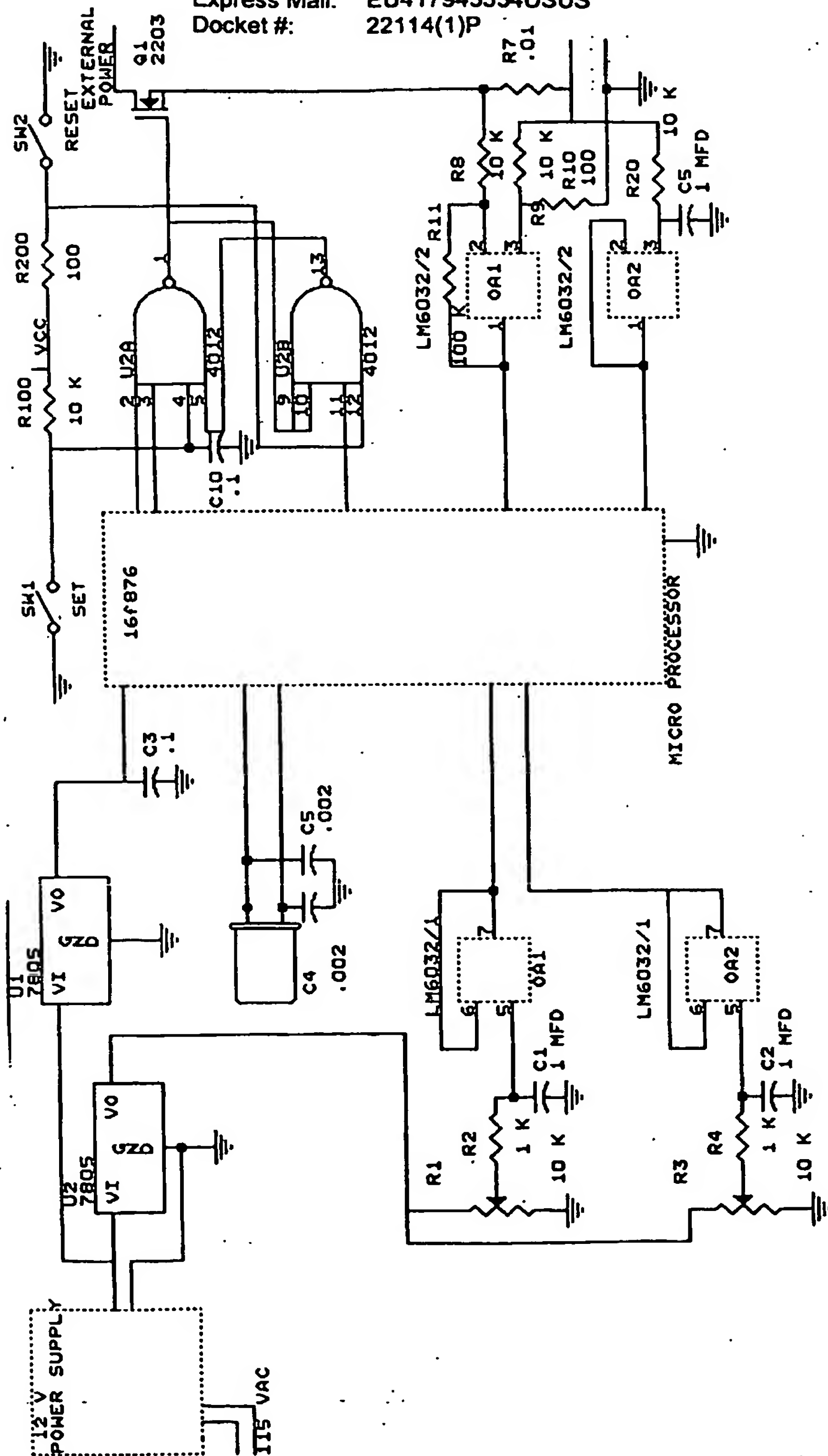Express Mail:  EU417945354USUS
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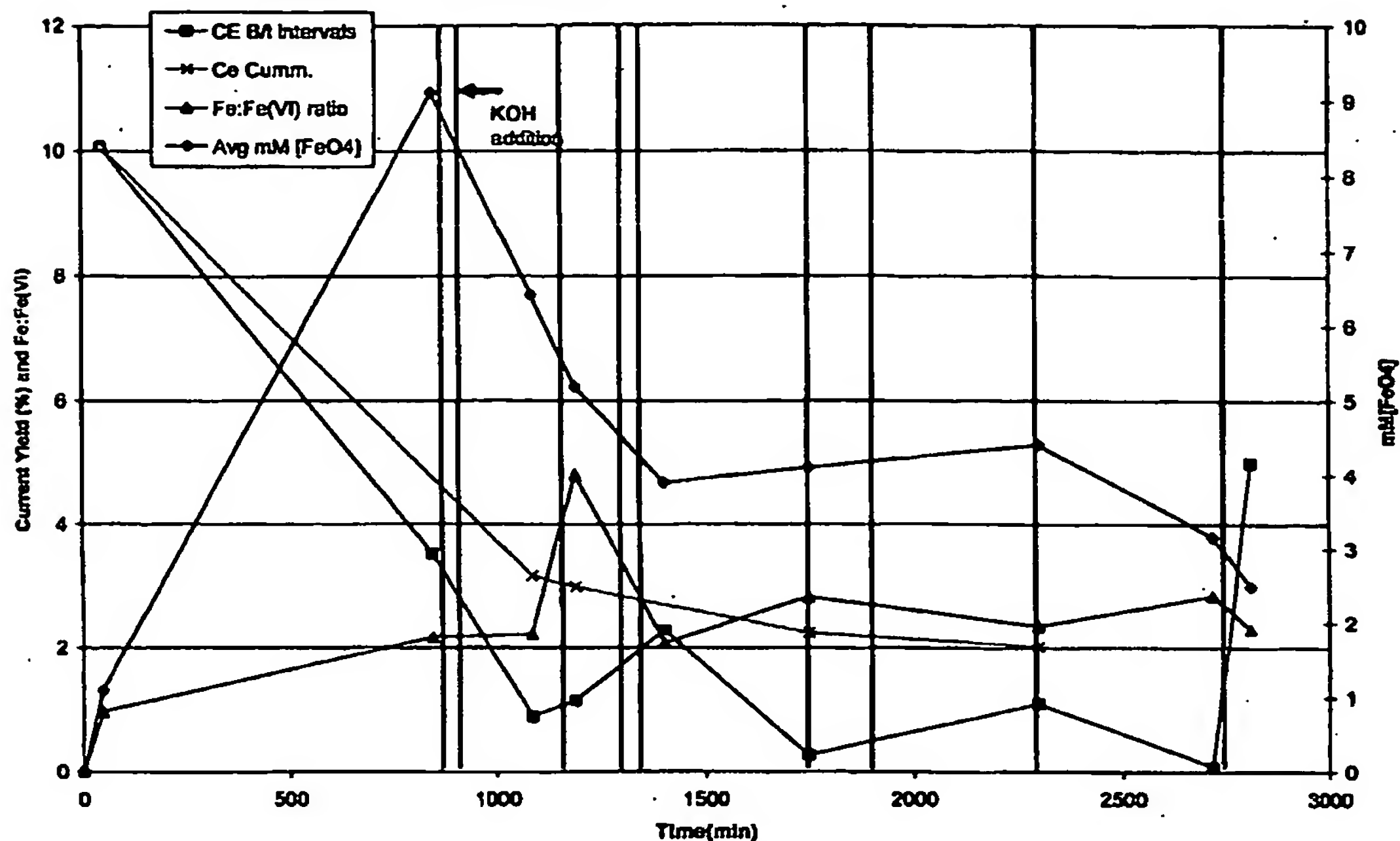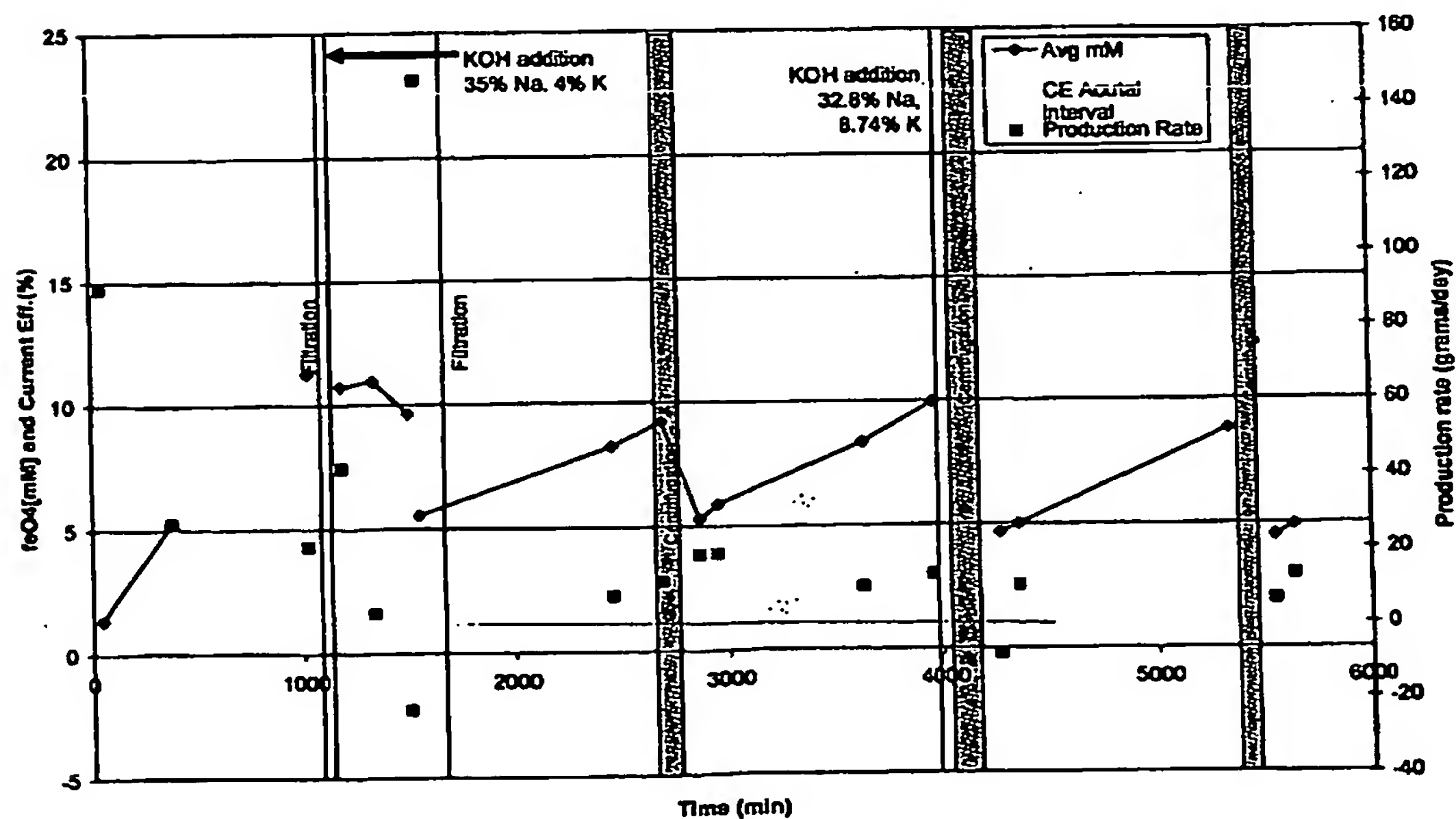
FIGURE 3



FIGURE 4

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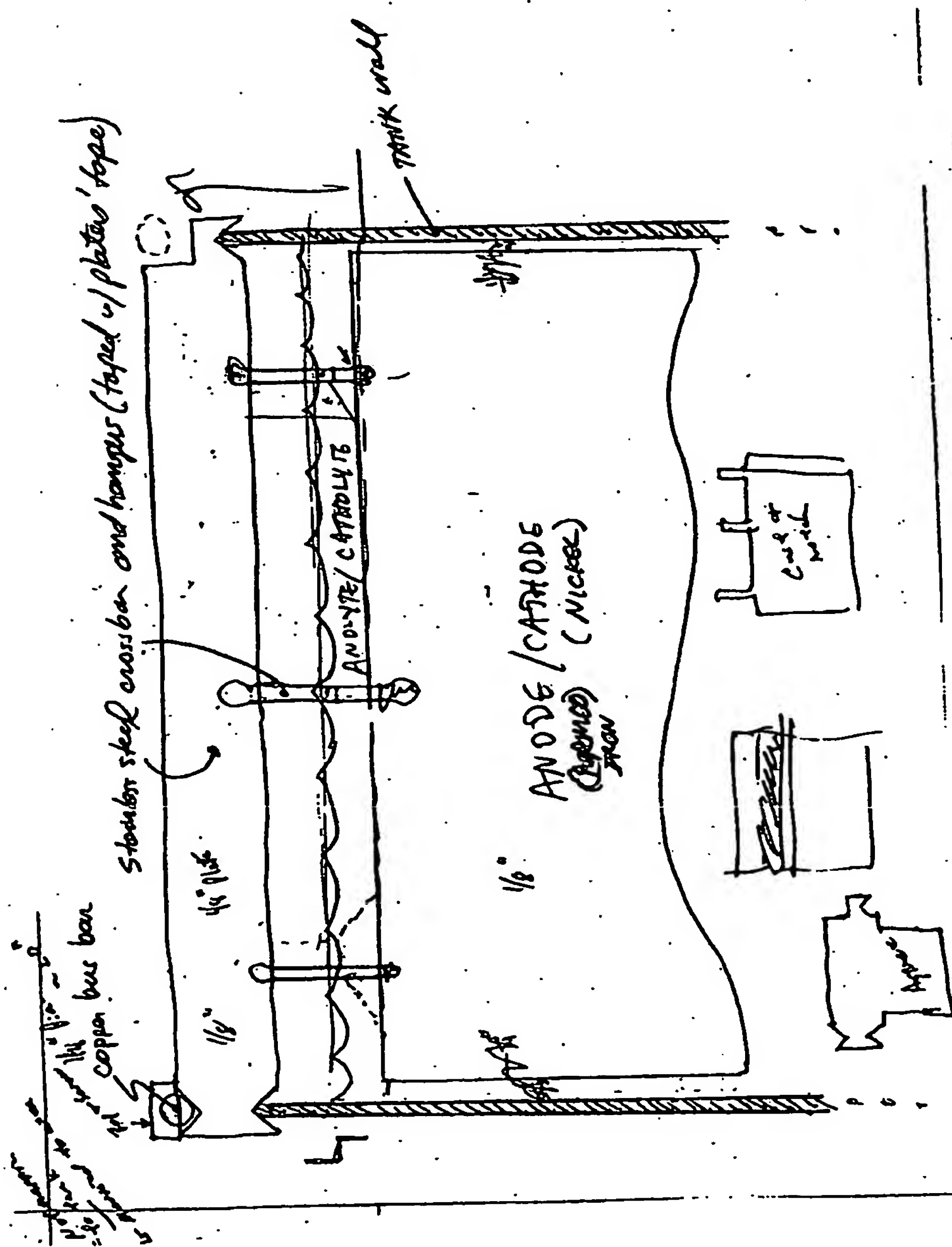Docket #:        22114(1)P
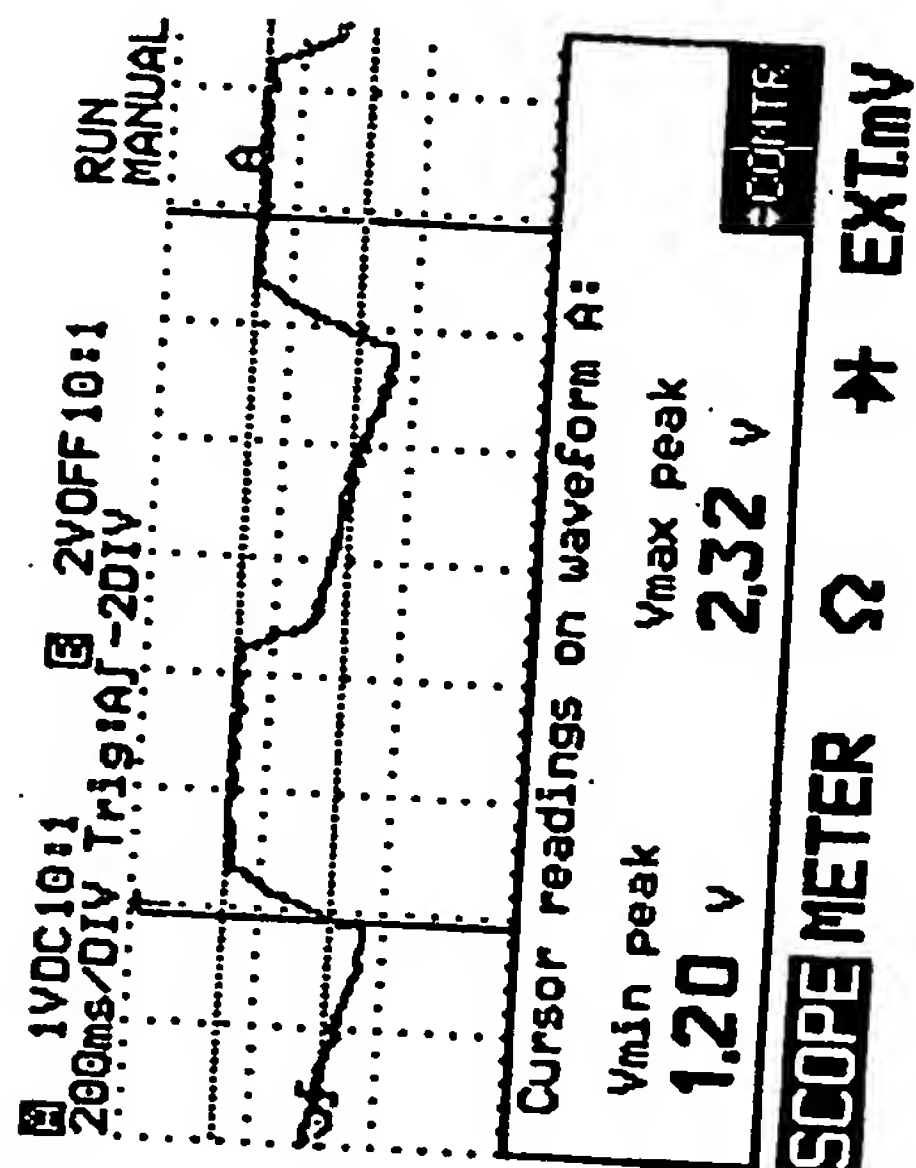


Figure 1: Representative waveform for ferrate production. Square wave form at 1hz with ~320ms high, and 80ms low.

FIGURE 5
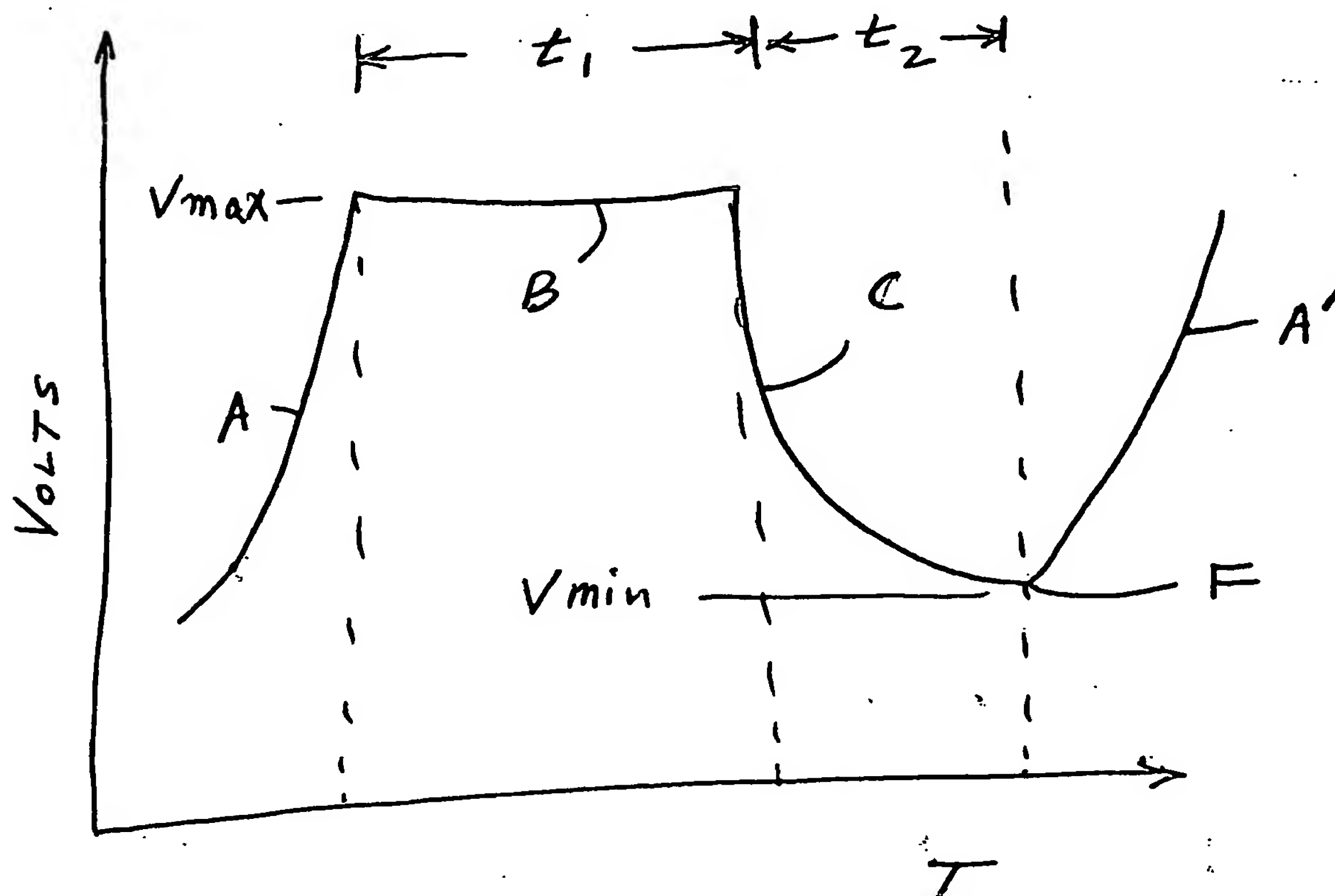
FIG. 5A
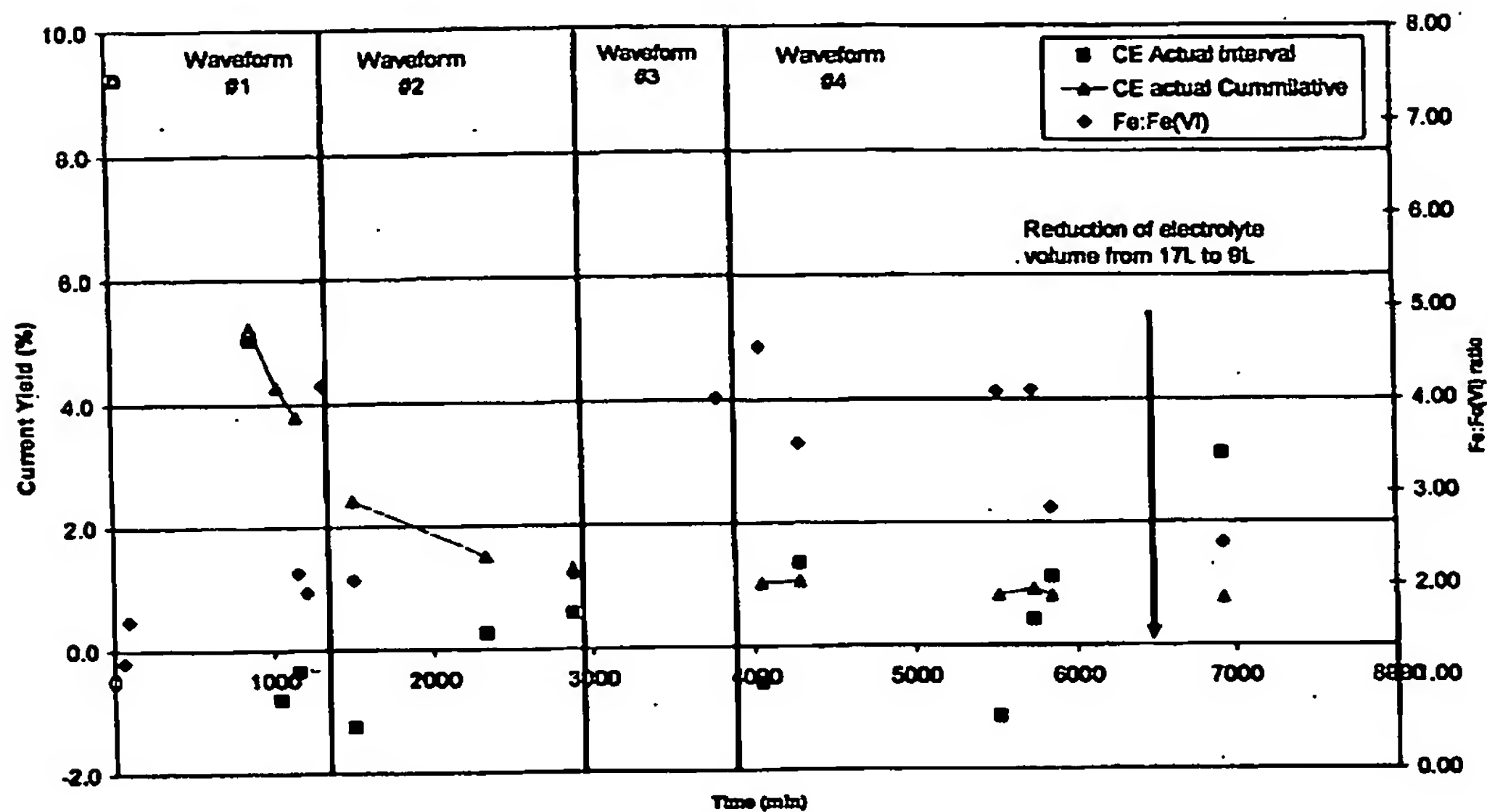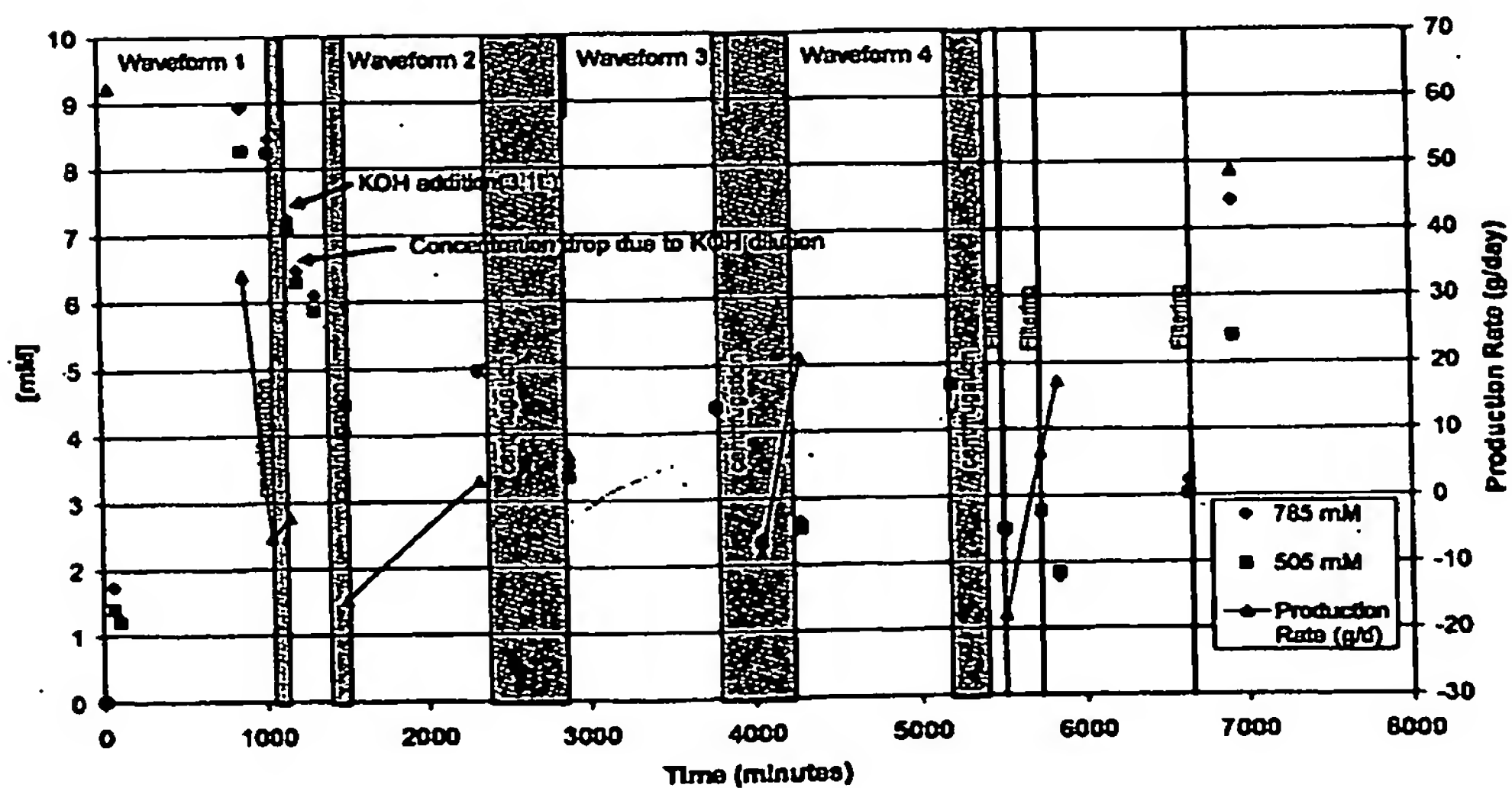
FIGURE 6



FIGURE 7

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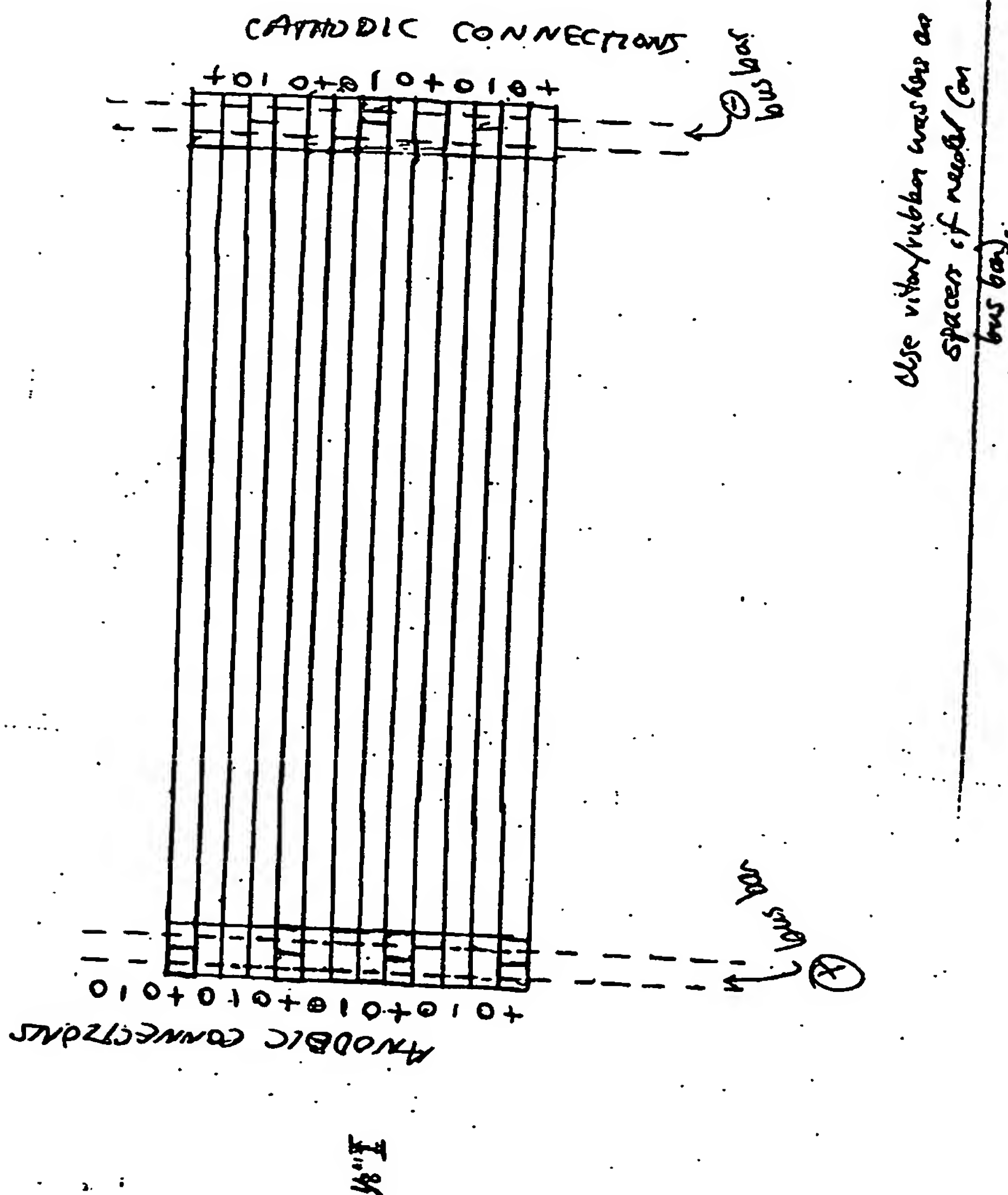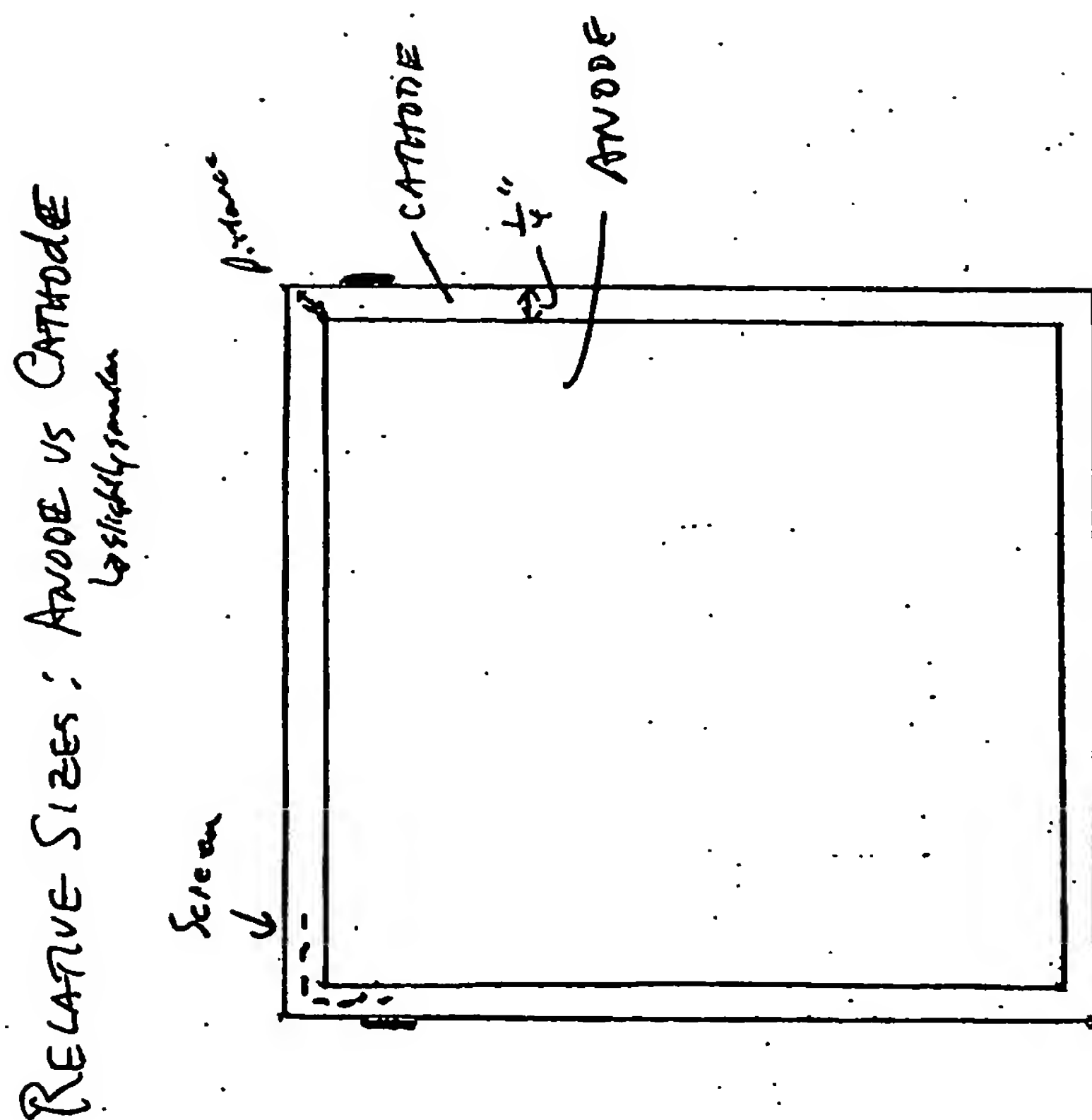Docket #:        22114(1)P

FIGURE 8



FIGURE 9

FIGURE 10



FIGURE 11

FIGURE 12



FIGURE 13

FIGURE 14

# FIGURE 15

Title:           **Apparatus for Producing Ferrate (VI) and Method for Producing Same**

Inventors:    **Monzyk, Bruce F., *et al.***

Attorney:      **Klaus H. Wiesmann, 614-424-6589**
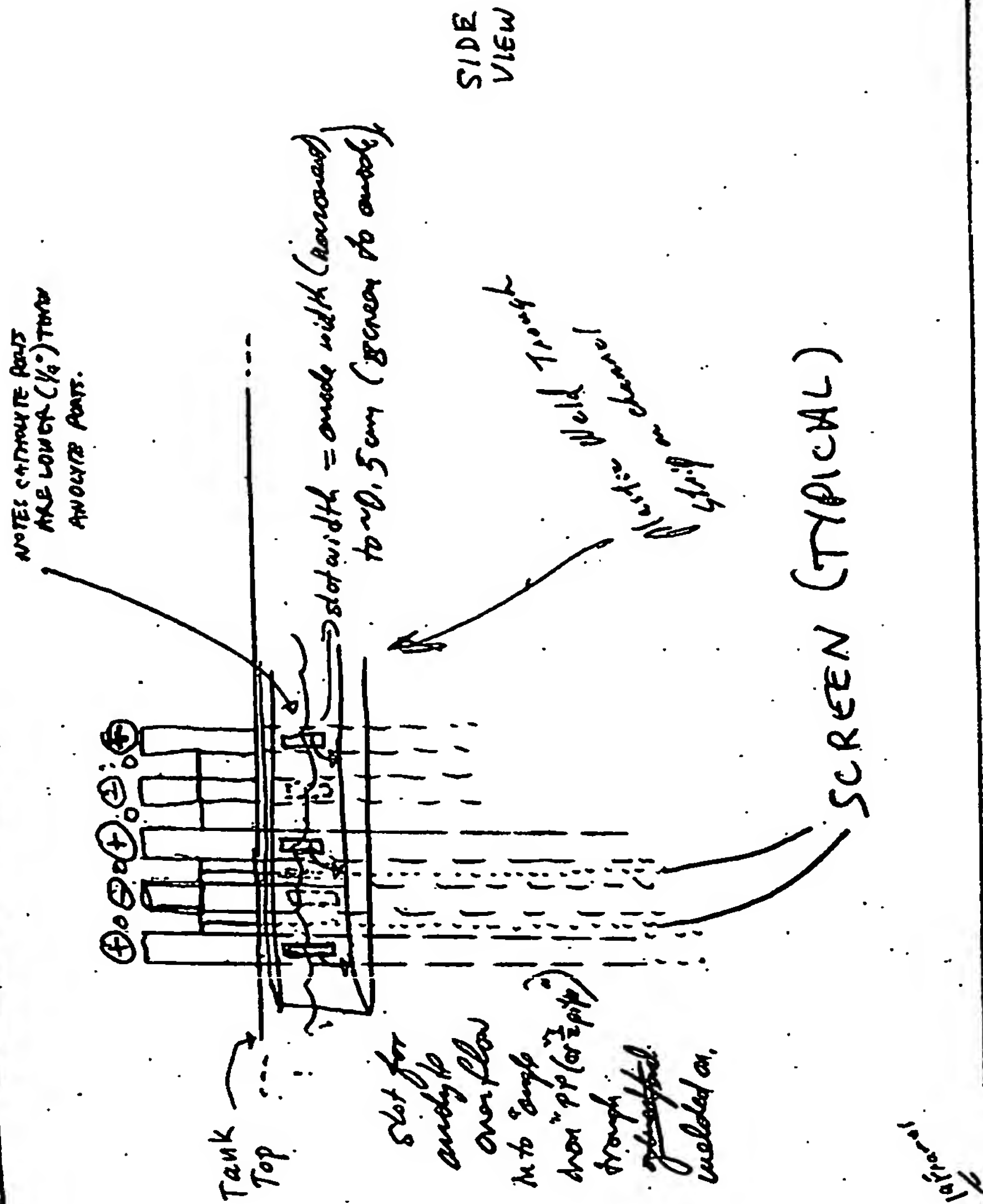
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Docket #:     **22114(1)P**

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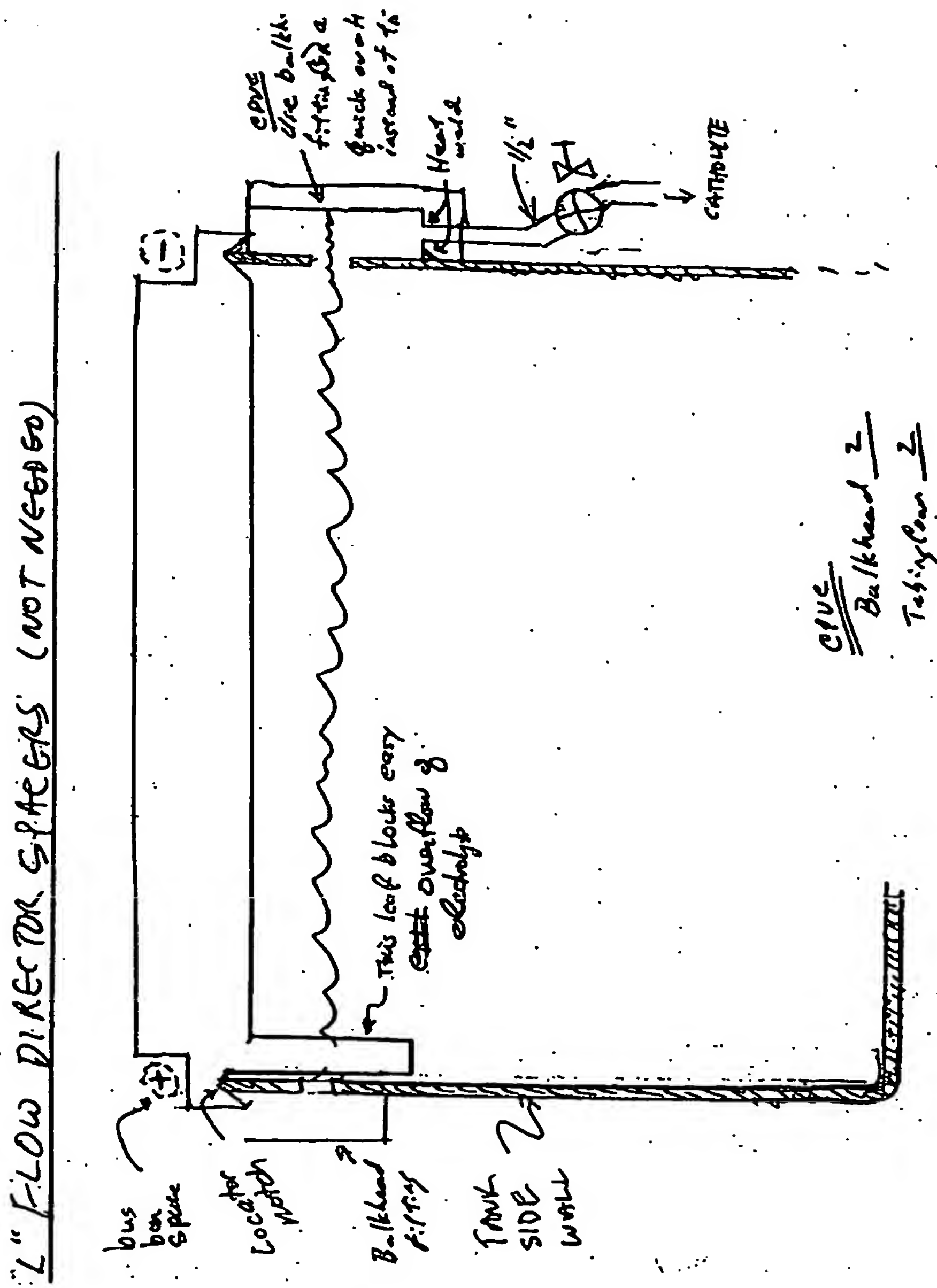Docket #: 22114(1)P

FIGURE 16

Legend: □ 785 Peak  △ 505 Peak  —●— CE (Interval)  —✕— CE Running Avg

Current Efficiency (%)
Ferrate Conc (mM)
Time (min)

FIGURE 17

FIGURE 18

**Centrifuged Ferrate Salt Composition as**
**Chemical Species Averages**
July 8-12, 2002

$K_2FeO_4$    Fe(III)    $CO_3^=$
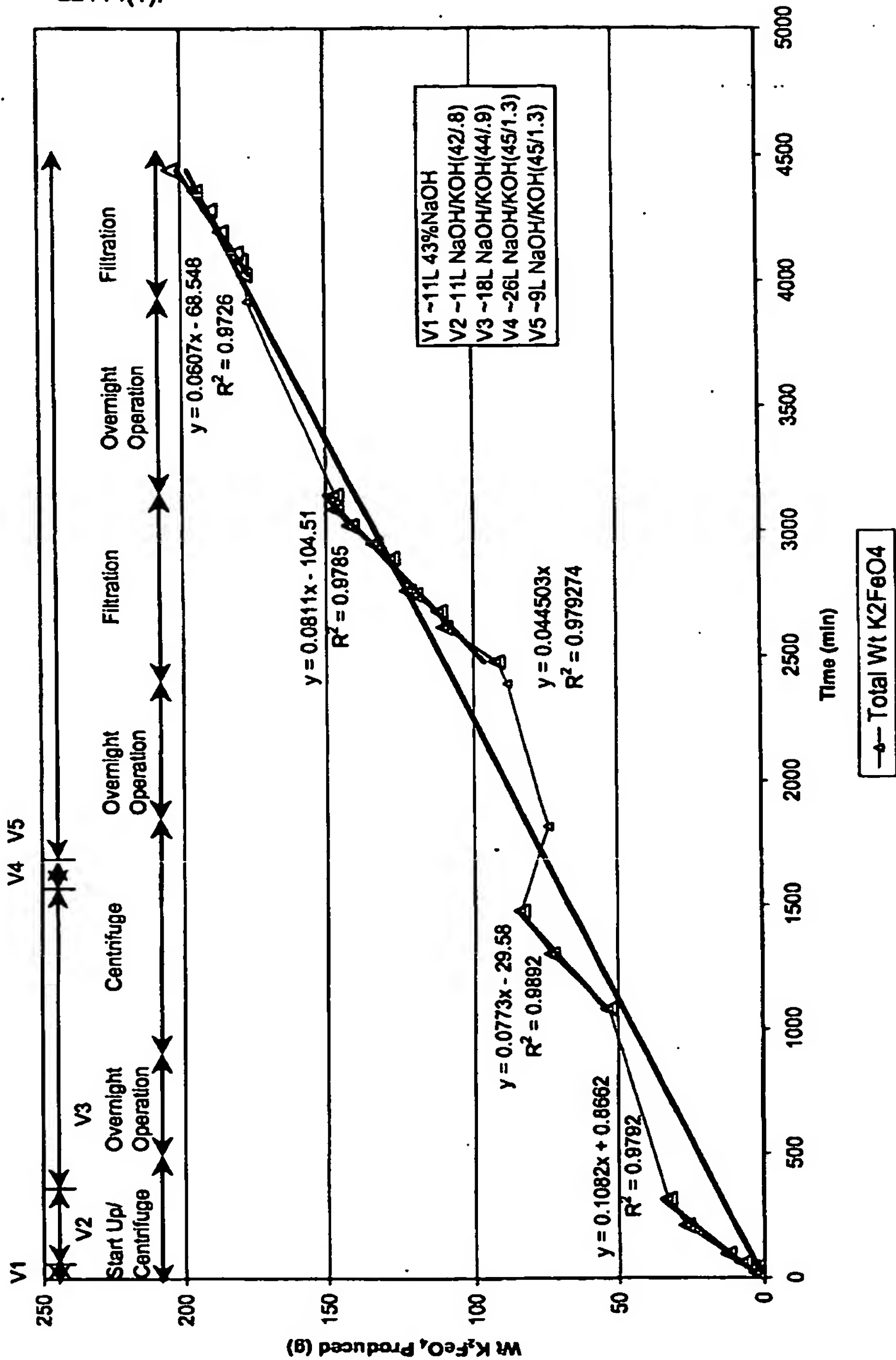
water

NaOH

- ■ wt% Water
- □ wt% NaOH
- ■ wt% K2FeO4
- ■ wt% Fe"(III)"
- ▨ wt % CO32-
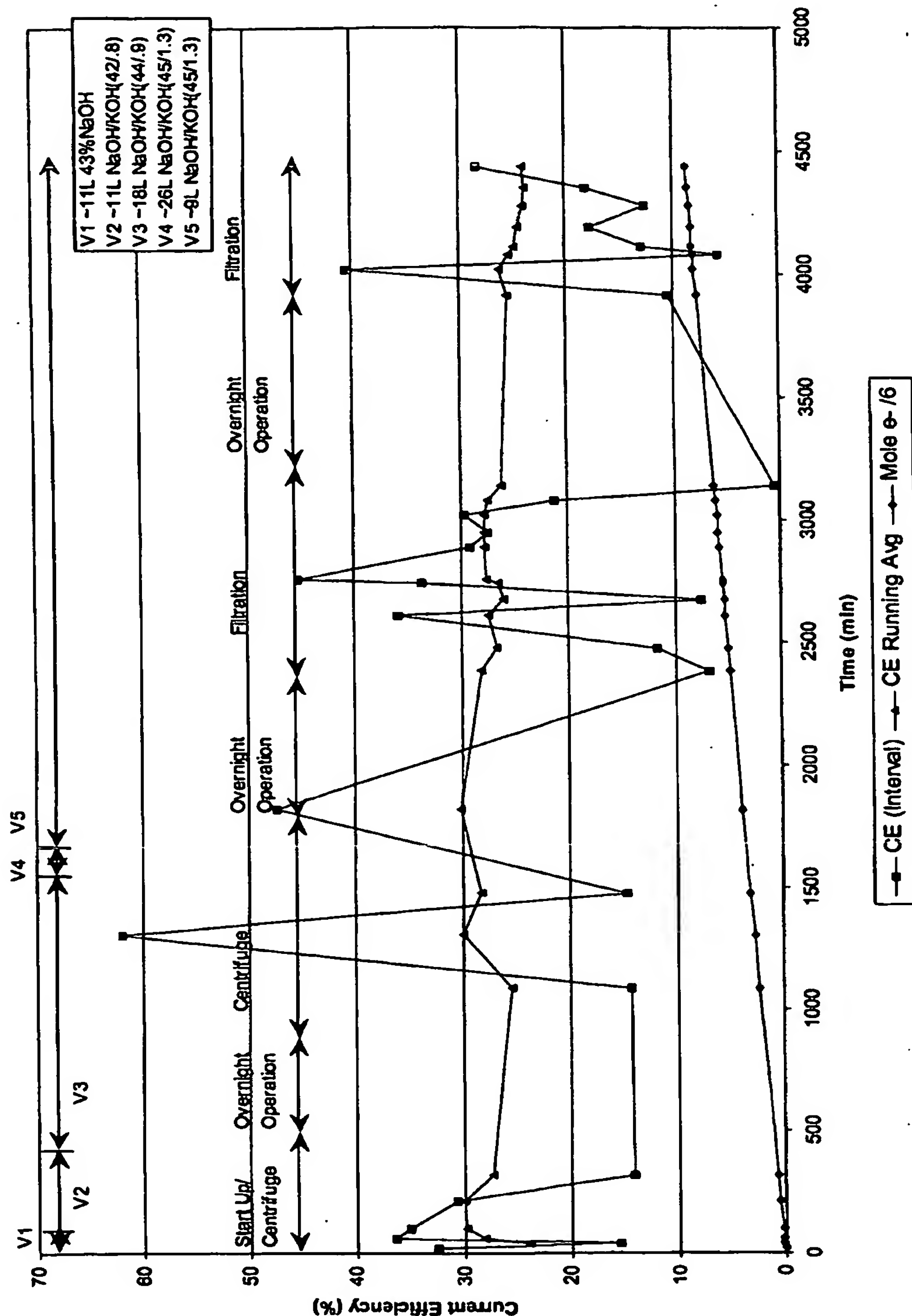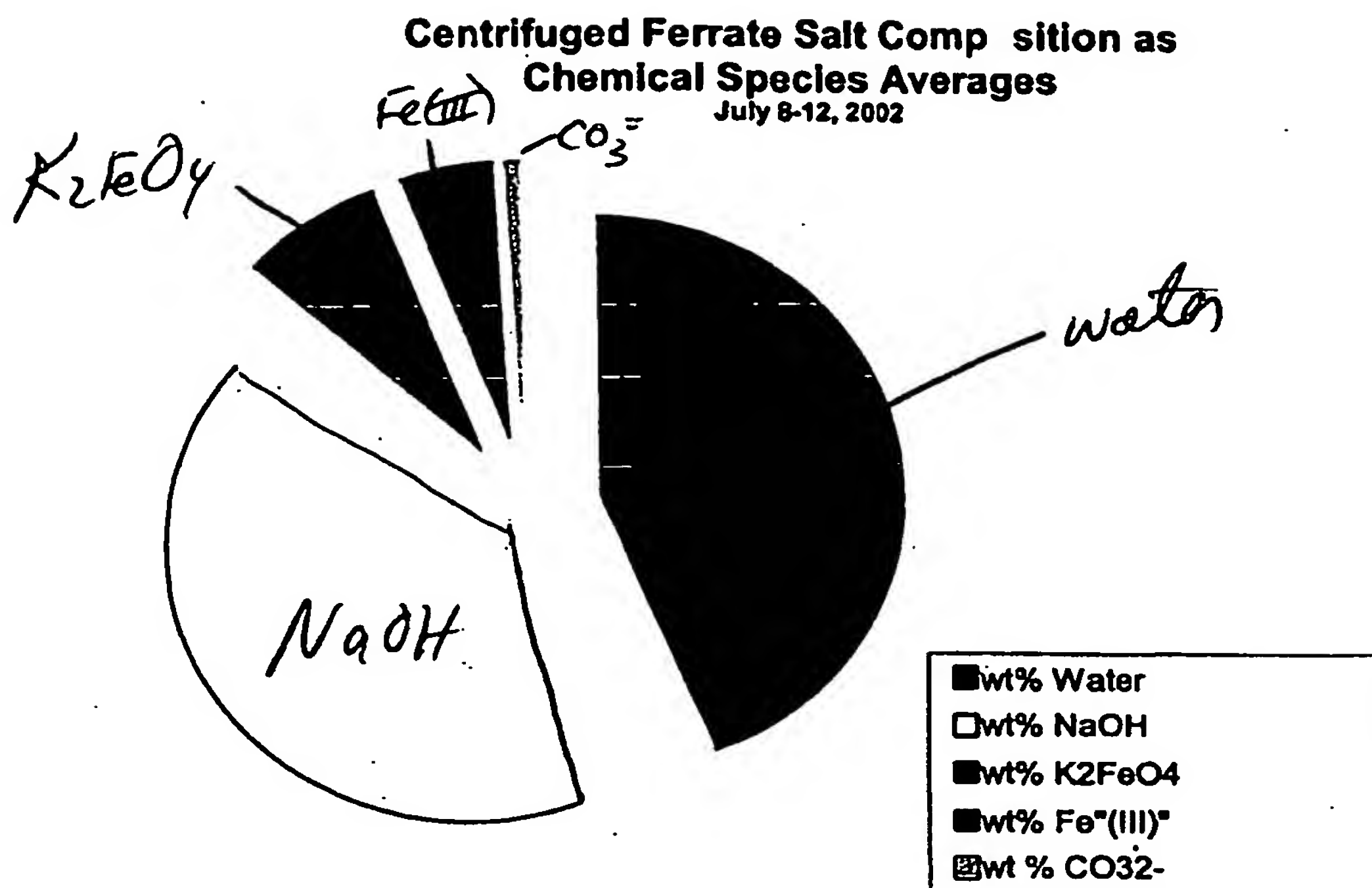
TABLE 6

| wt% Water | 43.04% |
|---|---|
| wt% NaOH | 41.56% |
| wt% $K_2FeO_4$ | 7.69% |
| wt% Fe"(III)" compounds | 4.86% |
| wt % $CO_3^{2-}$ | 0.74% |
| total | 97.89% |

*Removal of water and hydroxides from ferrate(VI) salts using centrifugation*

In this section, the ability of both centrifuges to remove water, sodium and potassium hydroxides is analyzed. As mentioned *h e r e i n* batch centrifugation was tested to see how ferrate(VI) would behave under these conditions. Two to three liters of electrolyte were removed at one time, centrifuged at 2500RPM in a 6x1L centrifuge for 20minutes. The solids were then collected by decanting the supernatant and then spun down again in a smaller 4x50ml centrifuge for 30minutes, further increasing the weight percentage of ferrate. There is a plot showing the percent solids in each of the centrifuged 1L bottles containing electrolyte and the concentration of ferrate(VI) in the solids. Table 6 shows the increase in weight percent ferrate(VI) after the second spin down in the 50ml Centrifuge.
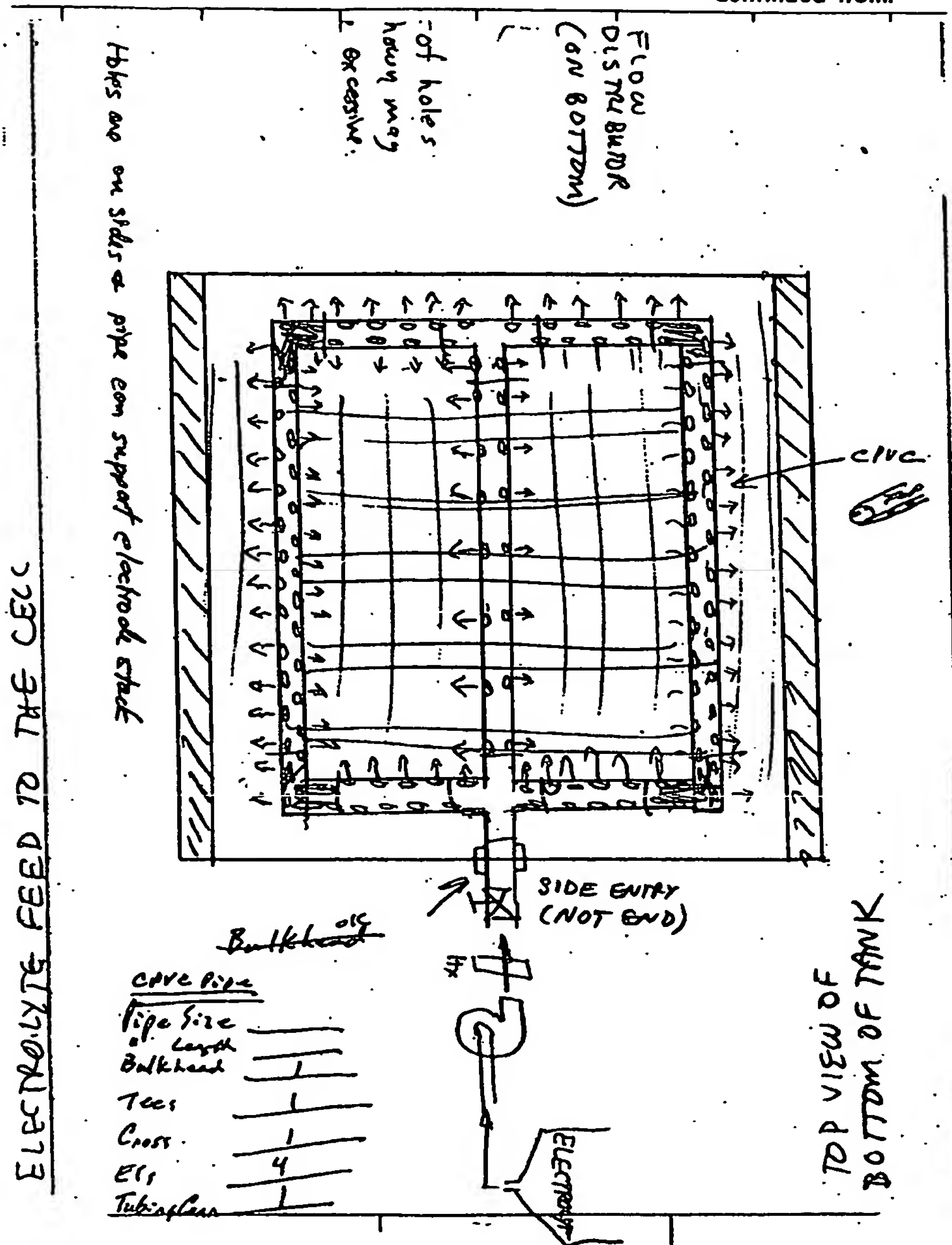
FIGURE 19

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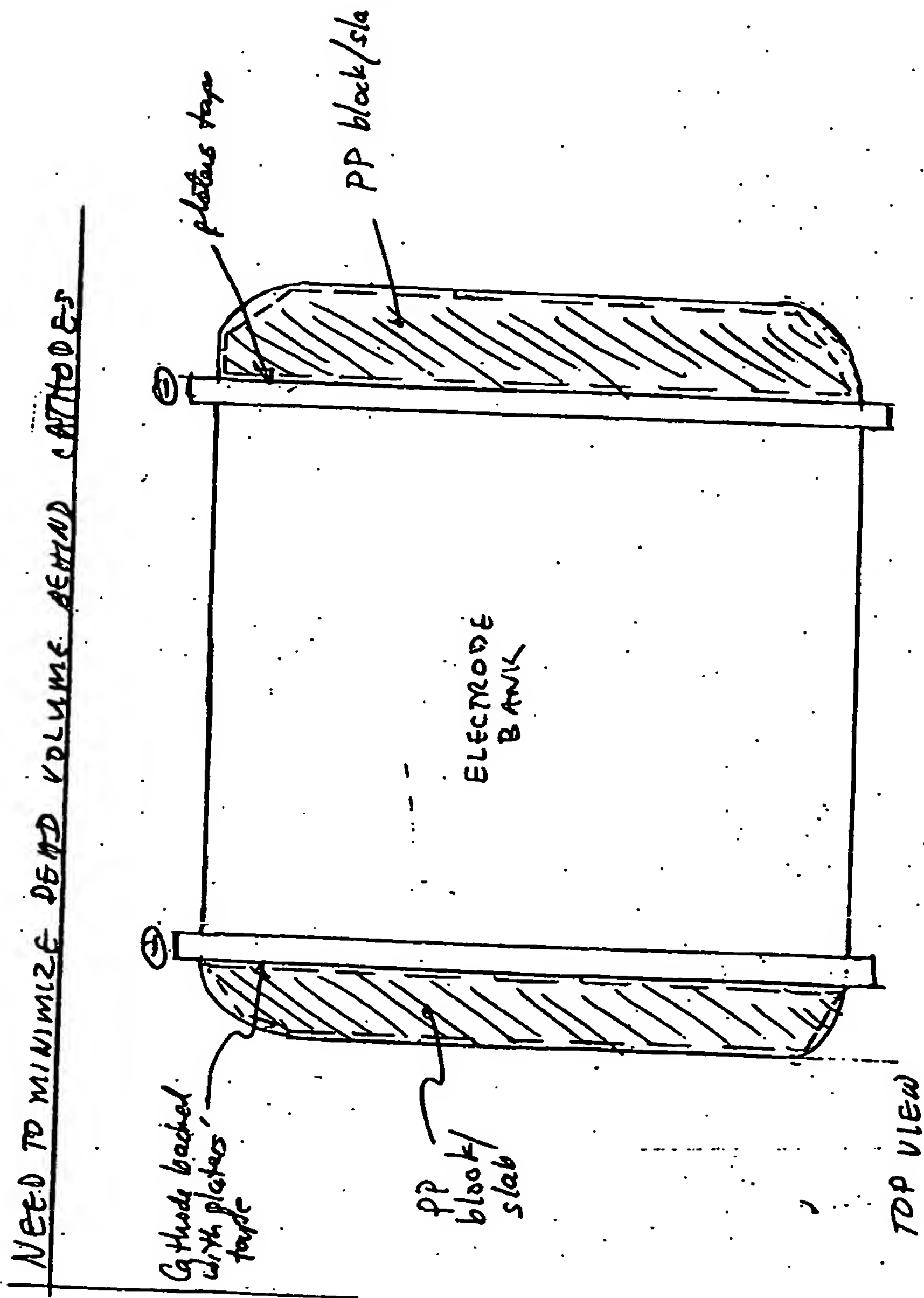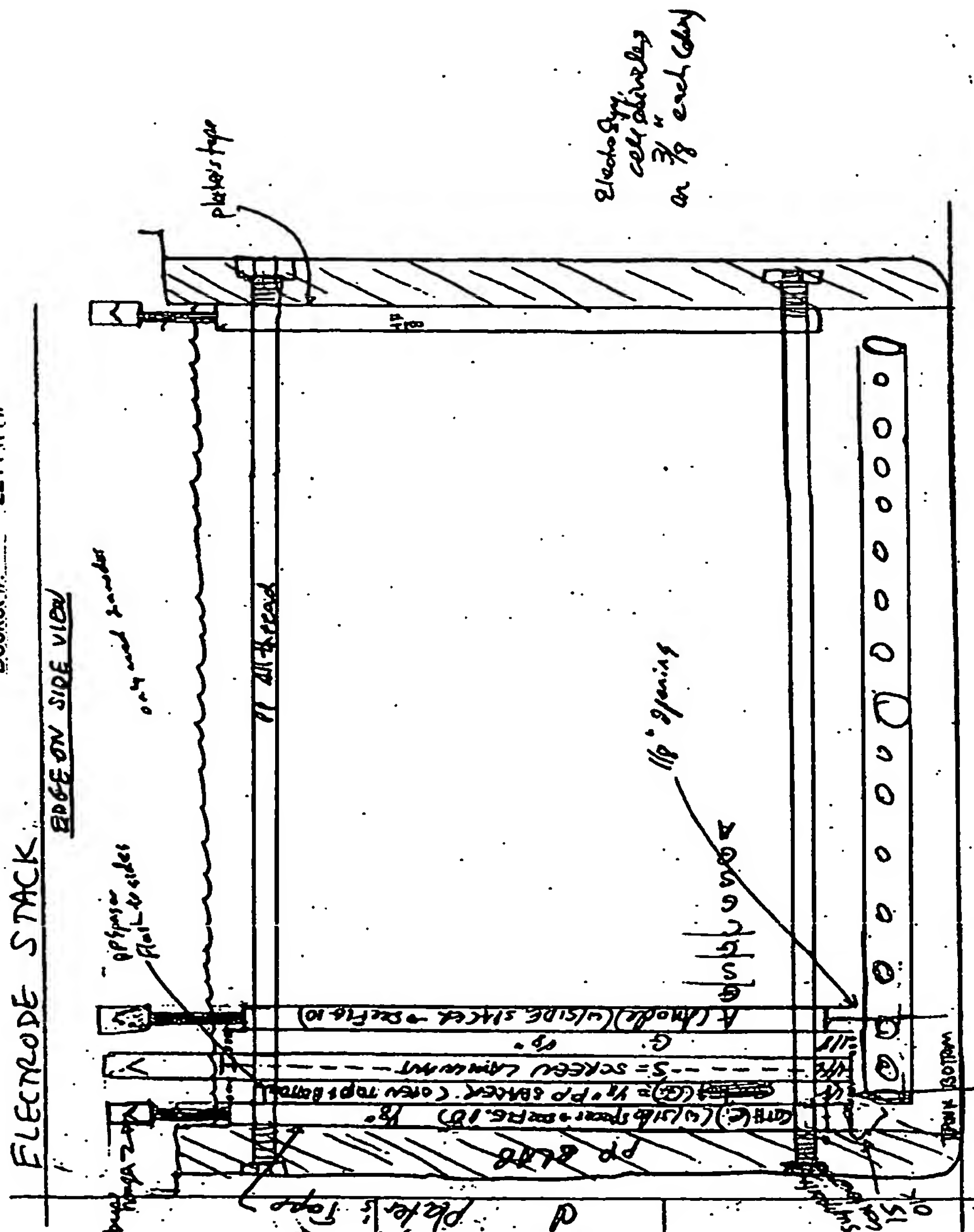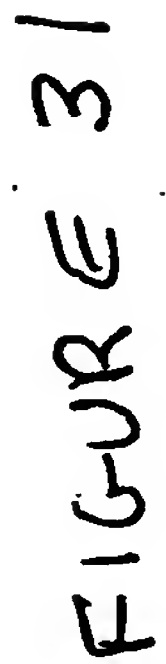Docket #:       22114(1)P

FIGURE 20

FIGURE 21

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Docket #:       22114(1)P

FIGURE 22

FIGURE 23

Title: Apparatus for Producing Ferrate (VI) and Method for
Producing Same
Inventors: Monzyk, Bruce F., *et al.*
Attorney: Klaus H. Wiesmann, 614-424-6589
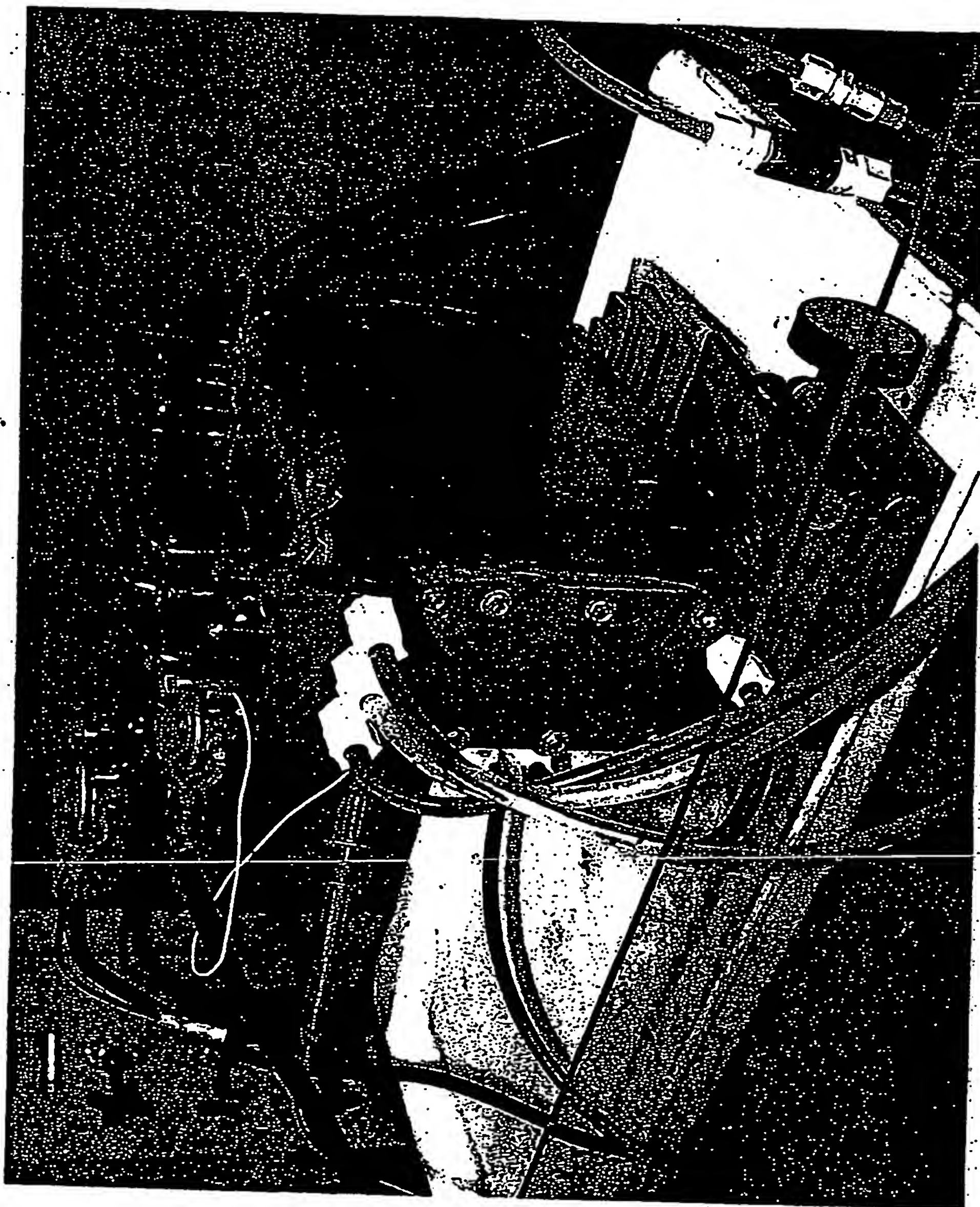Express Mail: EU417945354USUS
Docket #: 22114(1)P

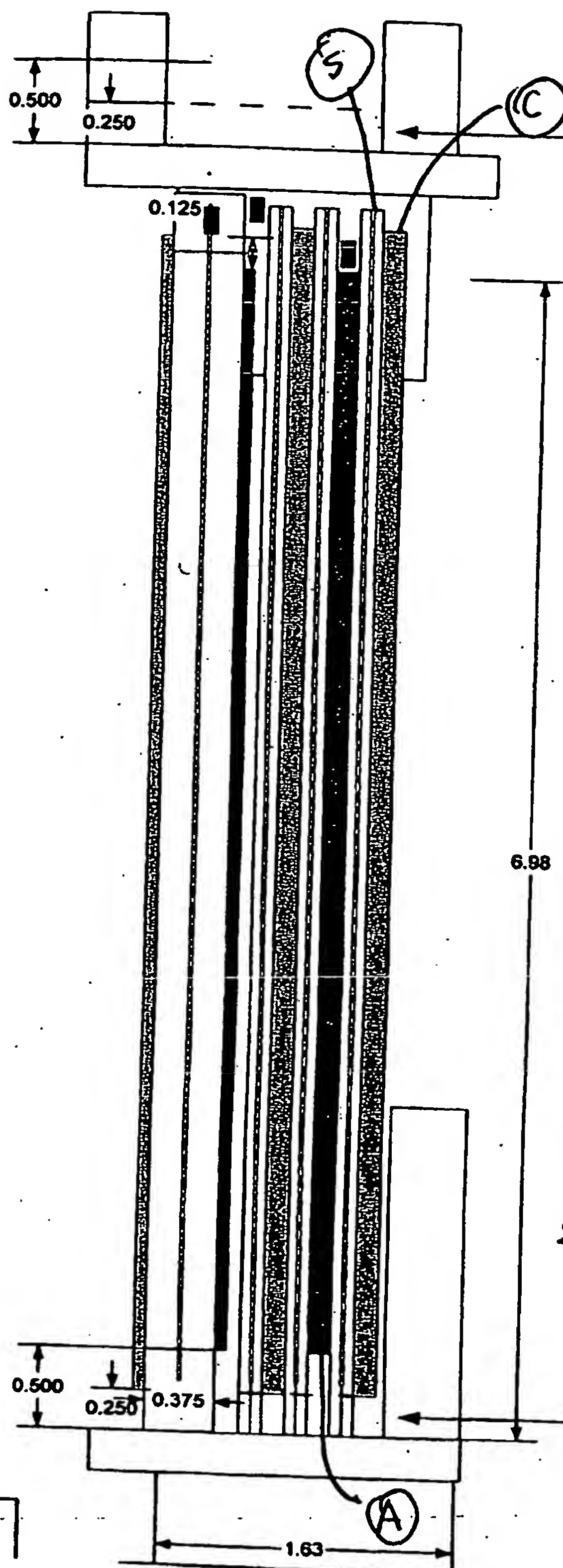FIGURE 24

Title:          Apparatus for Producing Ferrate (VI) and Method for
                Producing Same
Inventors:      Monzyk, Bruce F., *et al.*
Attorney:       Klaus H. Wiesmann, 614-424-6589
Express Mail:   EU417945354USUS
Docket #:       22114(1)P

RELATIVE SIZES: ANODE vs CATHODE
(slightly smaller)

CATHODE

ANODE

distance

$\frac{1}{2}$"

Screen

Top

FIGURE 25

FIGURE 26

Title:          Apparatus for Producing Ferrate (VI) and Method for
                  Producing Same
Inventors:    Monzyk, Bruce F., *et al.*
Attorney:    Klaus H. Wiesmann, 614-424-6589
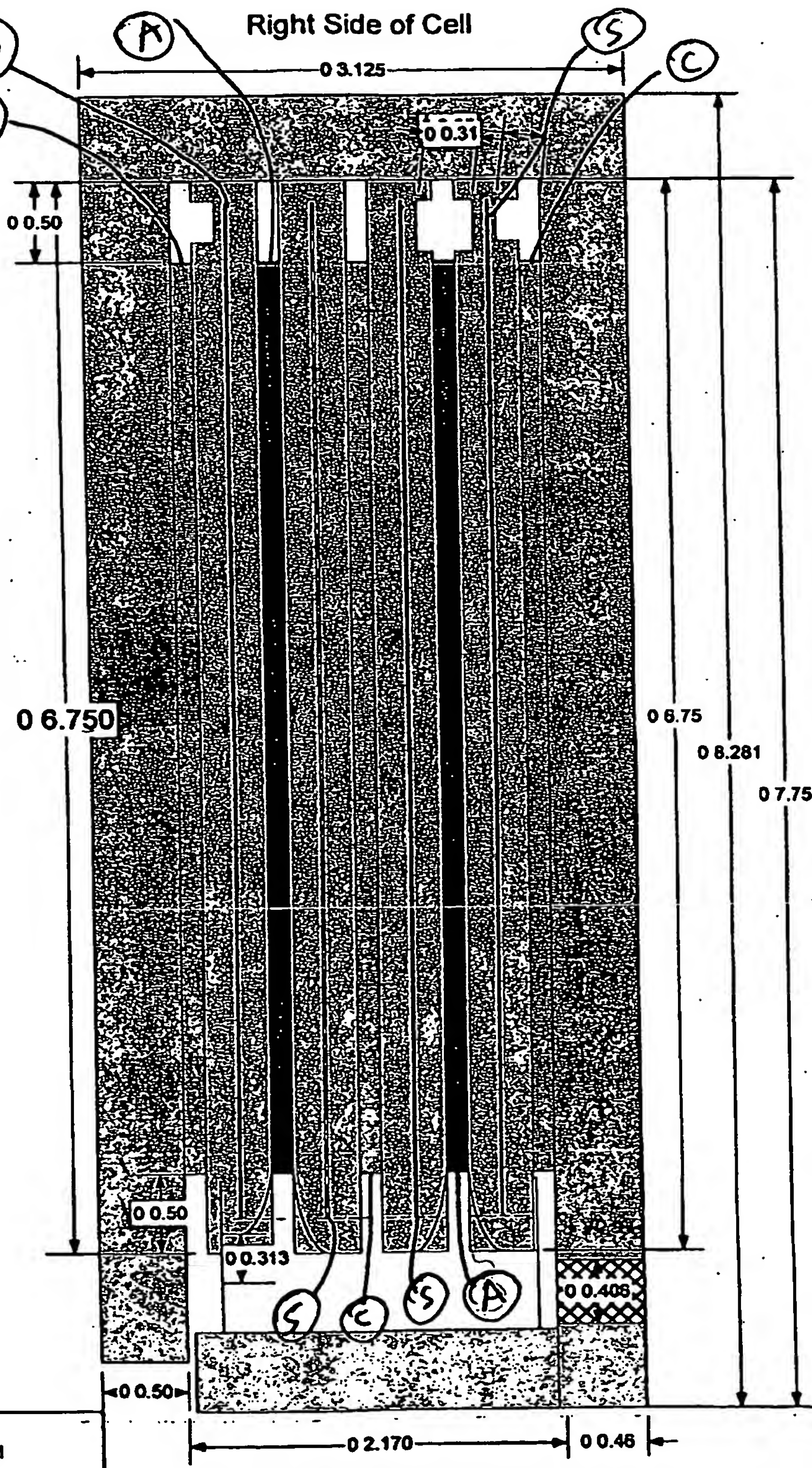Express Mail:  EU417945354USUS
Docket #:    22114(1)P

FIGURE 27

Title:  Apparatus for Producing Ferrate (VI) and Method for
        Producing Same
Inventors:  Monzyk, Bruce F., *et al.*
Attorney:  Klaus H. Wiesmann, 614-424-6589
Express Mail:  EU417945354USUS
Docket #:  22114(1)P

Continued from:



FIGURE 28

FIGURE 29

ELECTRODE STACK

EDGE ON SIDE VIEW

FIGURE 30

Title:          Apparatus for Producing Ferrate (VI) and Method for
                Producing Same
Inventors:      Monzyk, Bruce F., et al.
Attorney:       Klaus H. Wiesmann, 614-424-6589
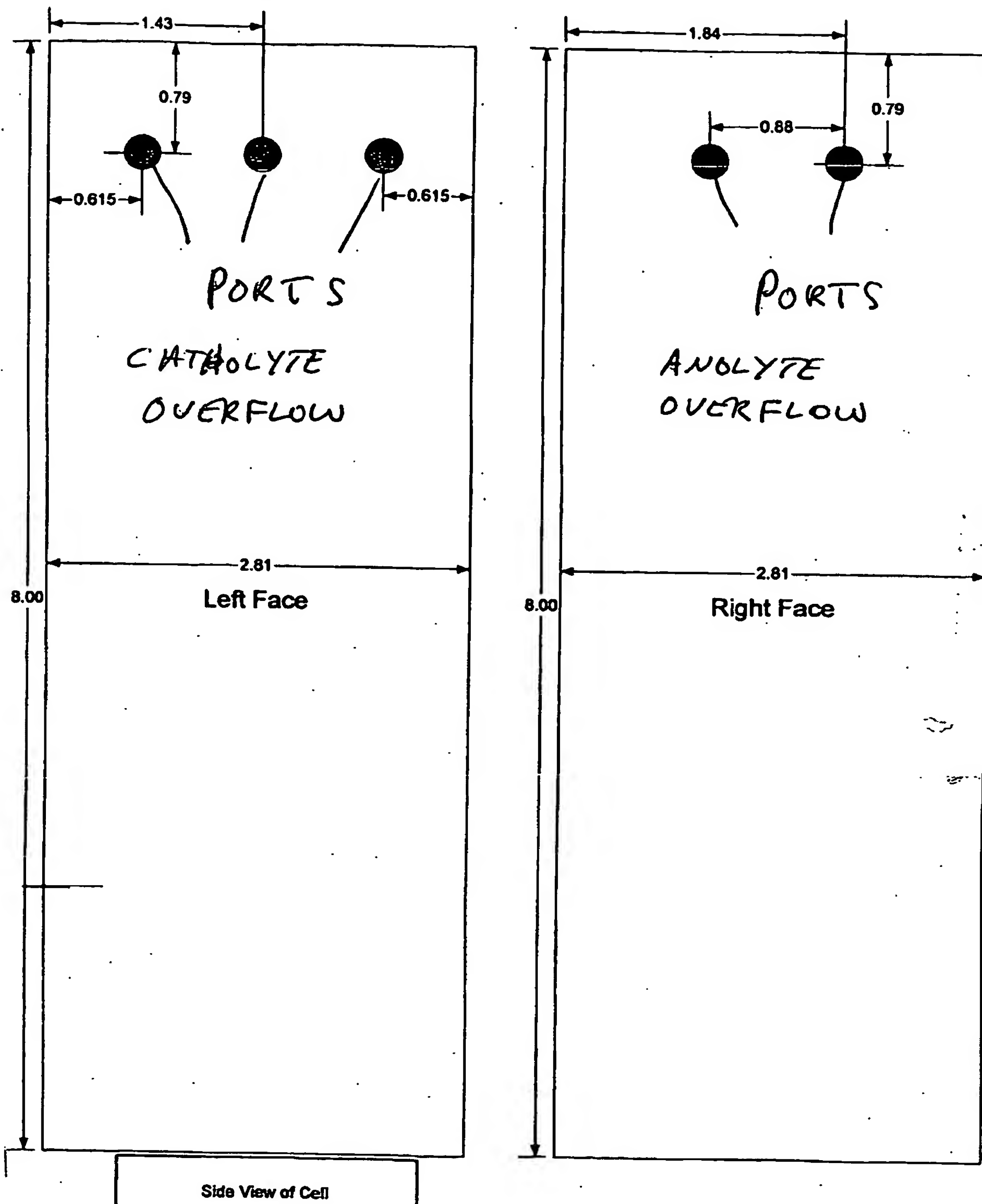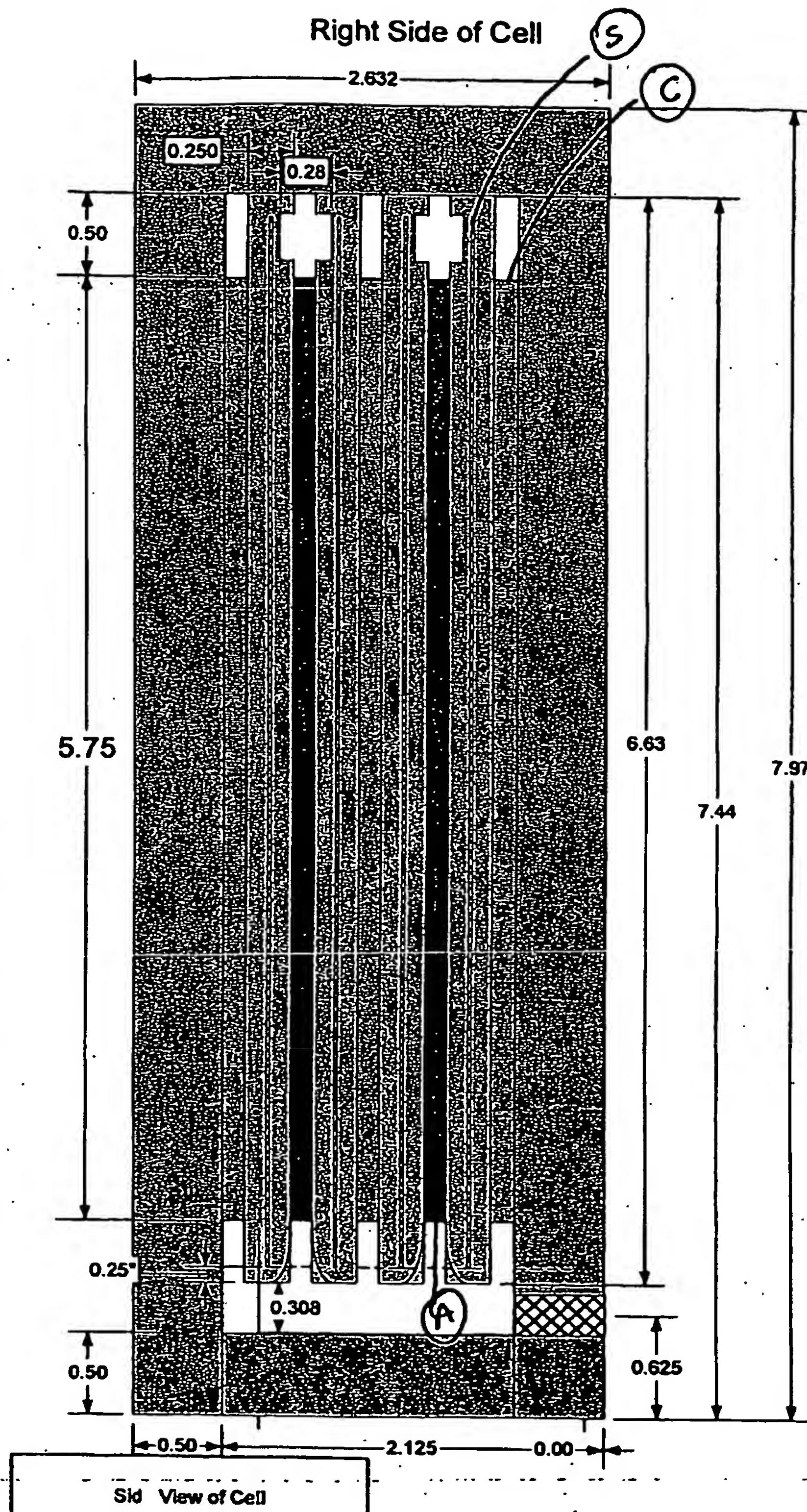Express Mail:   EU417945354USUS
Docket #:       22114(1)P

FIGURE 31

FIGURE 32

FIGURE 33

A = ANODE
C = CATHODE
S = SCREEN

C (TYPICAL MEASUREMENTS)

0.03in.
0.06
0.06in.
0.94

7.00
6.49

S TYPICAL

Side View f Cell

FIGURE 34

A = ANODE
C = CATHODE
S = SCREEN

0.500
0.250
0.125
6.98
0.500
0.250
0.375
1.63

Side View of Cell

**Right Side of Cell**

Ⓢ Ⓐ Ⓒ Ⓒ Ⓢ

O 3.125

O 0.31

O 0.50

O 6.750

O 6.75

O 8.281

O 7.75

O 0.50

O 0.313

Ⓢ Ⓒ Ⓢ Ⓐ

O 0.406

O 0.50

O 2.170

O 0.46

**Side View of Cell**

A = ANODE
C = CATHODE
S = SCREEN

FIGURE 35

PORTS

CATHOLYTE

OVERFLOW

Left Face

PORTS

ANOLYTE

OVERFLOW

Right Face

FIGURE 36

Side View of Cell

**Right Side of Cell**

S

C

2.632

0.250

0.28

0.50

5.75

6.63

7.44

7.97

0.25"

0.308

A

0.50

0.625

0.50

2.125

0.00

Sid  View of Cell

FIGURE 37

A = ANODE

C = CIATHODE

S = SCREEN

Ferrate(VI) spectra
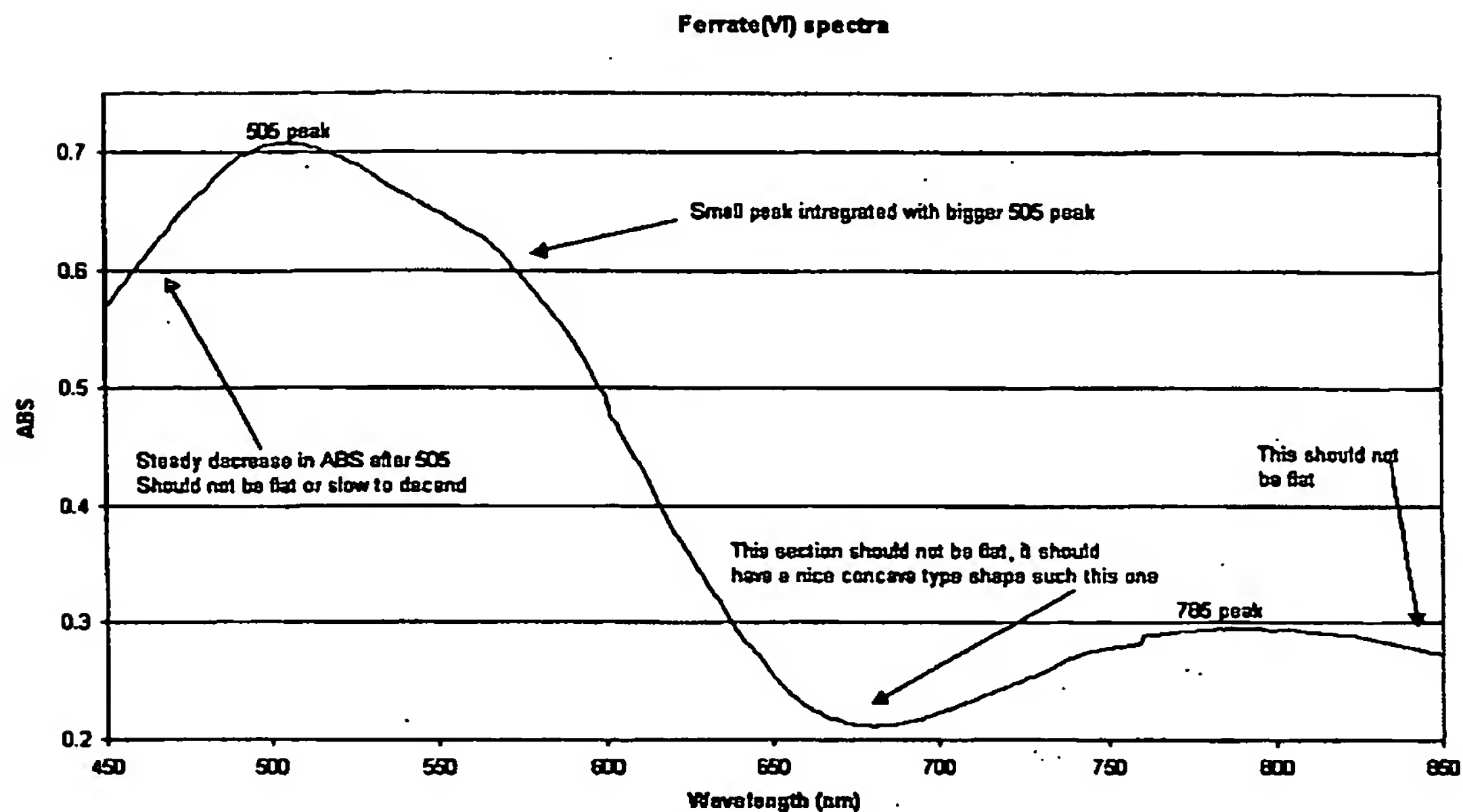


FIGURE 38

Title:       Apparatus for Producing Ferrate (VI) and Method for
             Producing Same
Inventors:   Monzyk, Bruce F., et al.
Attorney:    Klaus H. Wiesmann, 614-424-6589
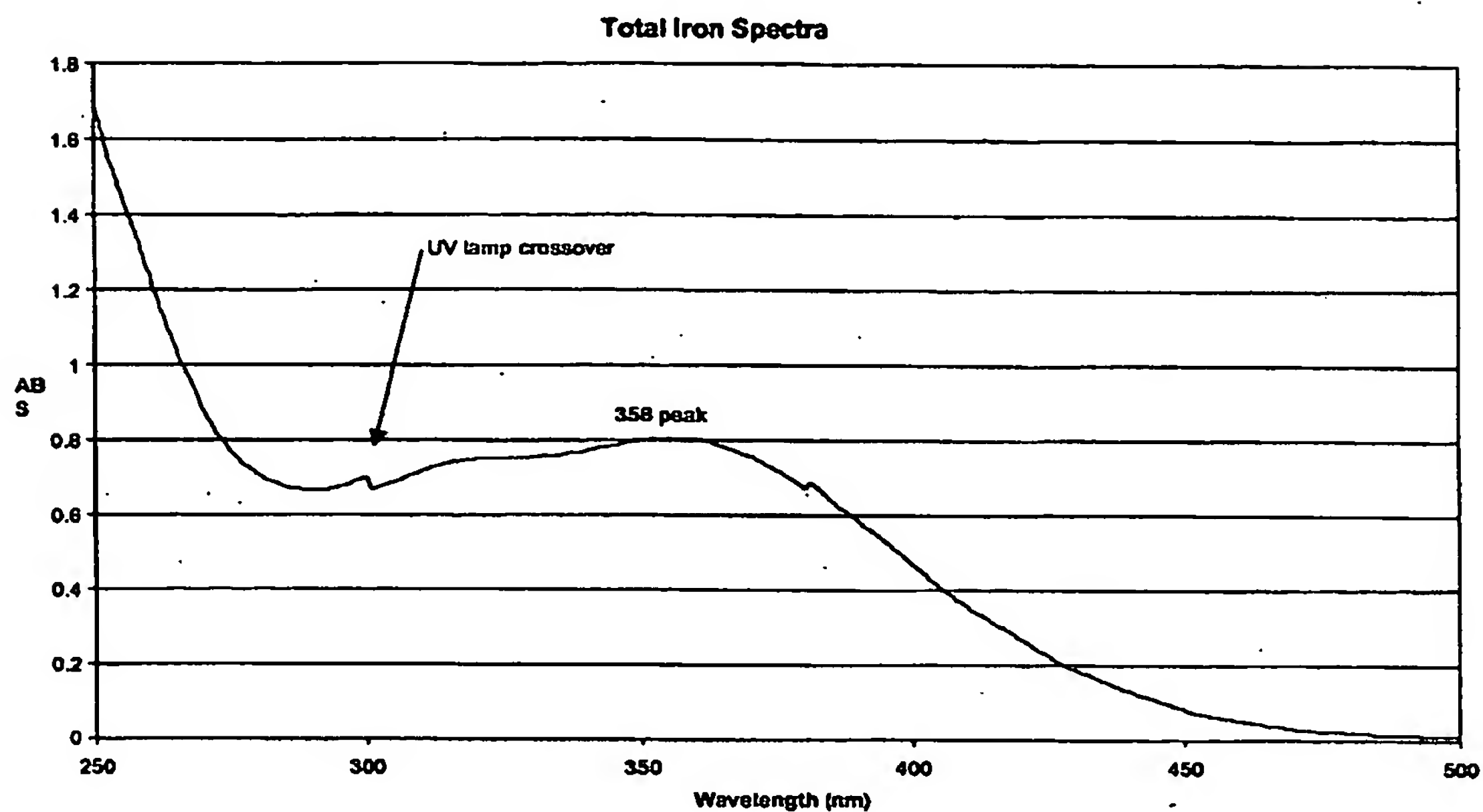Express Mail: EU417945354USUS
Docket #:    22114(1)P

**Total Iron Spectra**



FIGURE 39